Baton Rouge Consolidated Air Database Study

Albert Hendler, URS Corporation June 16, 2005



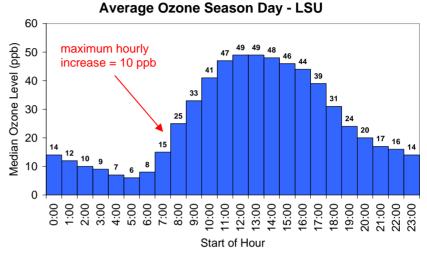
CAD Study Objectives

- Perform a statistical study of the Consolidated Air Database (CAD) to help identify the causes of 1-hour and 8-hour ozone exceedances in the Baton Rouge Nonattainment Area (Emphasis on Ozone Spikes)
 - Statistical Analysis of Ozone Spikes
 - Relationship to 1-hour and 8-hour exceedances
 - Frequency of occurrence and trends
 - Relationship to VOC, NOx, and weather parameters
 - Relationship to speciated VOC
 - VOC Levels and Reactivity
 - Reactivity-weighted concentrations and contributions to total reactivity
 - Spatial and temporal variations
 - Relationship to ozone spikes
 - Emissions
 - Reconciling ambient monitoring data with emissions estimates
 - Source-receptor relationships
 - Recommended Improvements to the Ozone Forecasting System

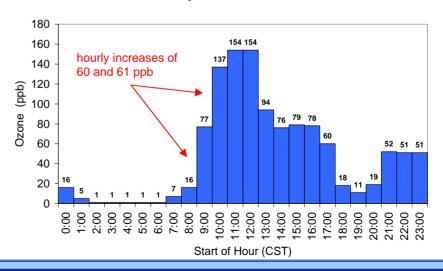


Analysis of Ozone Spikes

- No universally accepted definition for "ozone spike"
- Generally, a sudden rise in ozone level that is sometimes (but not always) followed by a sudden fall in ozone level
- Sometimes called Transient High Ozone Event (THOE)
- Texas SIP refers to Sudden
 Ozone Concentration
 Increase (SOCI), defined as
 a "hour-to-hour increase of
 40 ppb"



Ozone Spike - LSU 9/11/02

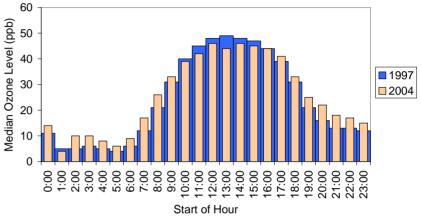




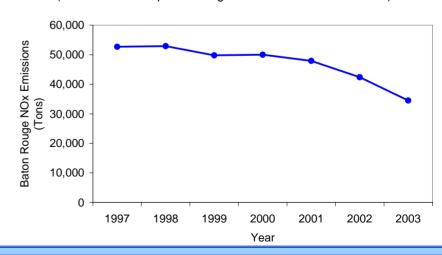
Is the Average Diurnal Variation Changing Over Time?

- 2004 average midday peak at LSU was 2 – 5 ppb lower than average midday peak in 1997
- Evening, nighttime, and early morning average ozone was up to 6 ppb higher in 2004 compared with 1997 averages
- Flattening of diurnal variation could be in response to NOx reductions
 - Less ozone formation during the day
 - Less ozone destruction at night

Average Ozone Season Diurnal Variation



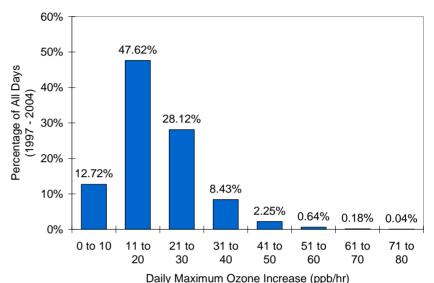
Baton Rouge Point Source NOx Emissions (Source: www.deq.louisiana.gov/evaluation/eis/eisdata.htm)

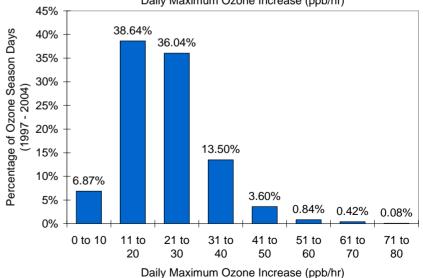




Frequency of Occurrence

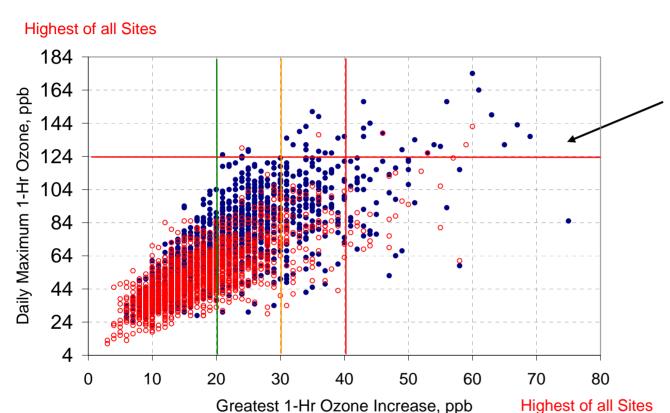
- About 3% of all days and 5% of ozone season days had hour to hour ozone concentration increases > 40 ppb/hr
- About 11% of all days and 18% of ozone season days had hour to hour ozone increases > 30 ppb/hr
- Most days had maximum hour to hour ozone increases between 11 ppb/hr and 30 ppb/hr







Relationship between Sudden Ozone Concentration Increases and Daily Max 1-Hr Ozone Levels



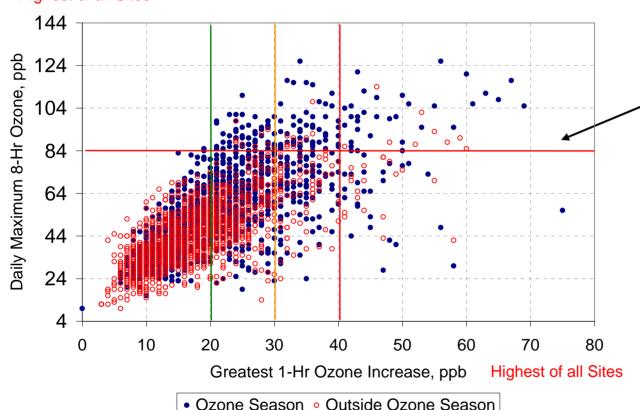
Hour to hour ozone increases of greater than 40 ppb occurred on about 50% of the 1-hour exceedance days





Relationship between Sudden Ozone Concentration Increases and Daily Max 8-Hr Ozone Levels

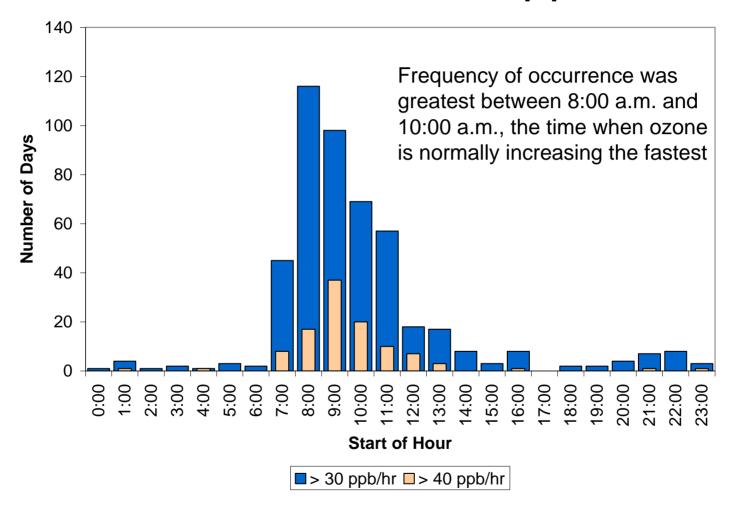
Highest of all Sites



Hour to hour ozone increases of greater than 40 ppb occurred on about 25% of the 8-hour exceedance days



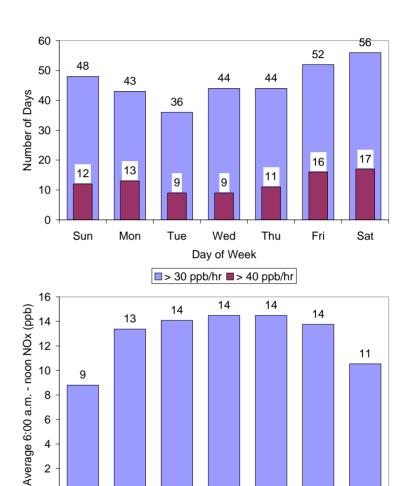
Times of Day when Ozone Increases Exceeded 30 and 40 ppb/hr





Weekly Patterns

- Frequencies of occurrence were greatest on Fridays and Saturdays
- This pattern does not appear to be caused by weekly patterns in ambient NOx levels



Sun

Mon

Tue

Wed

Day of Week

Thu

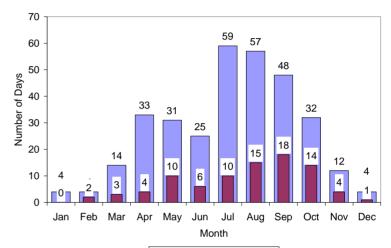


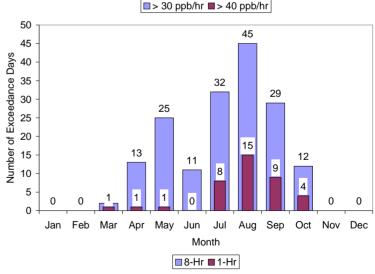
Sat

Fri

Seasonal Patterns

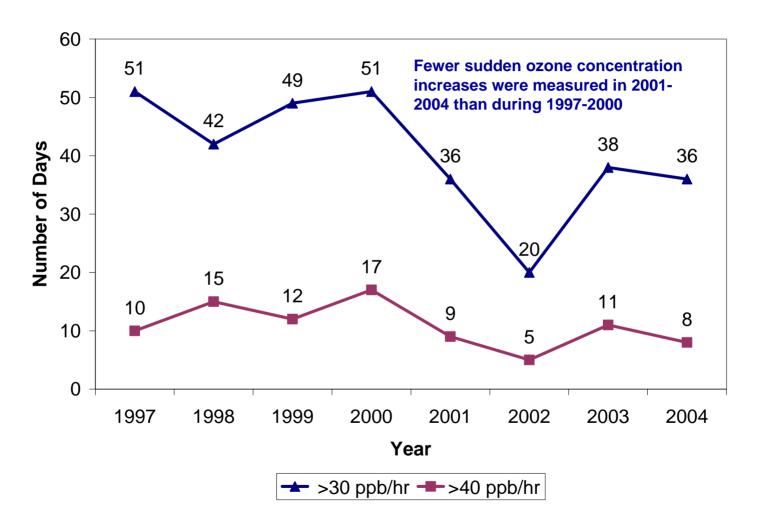
- Frequencies of occurrence were greatest during July – October, with secondary peak during April - June
- This pattern mirrors the monthly occurrences of 1-hour and 8-hour ozone exceedance days





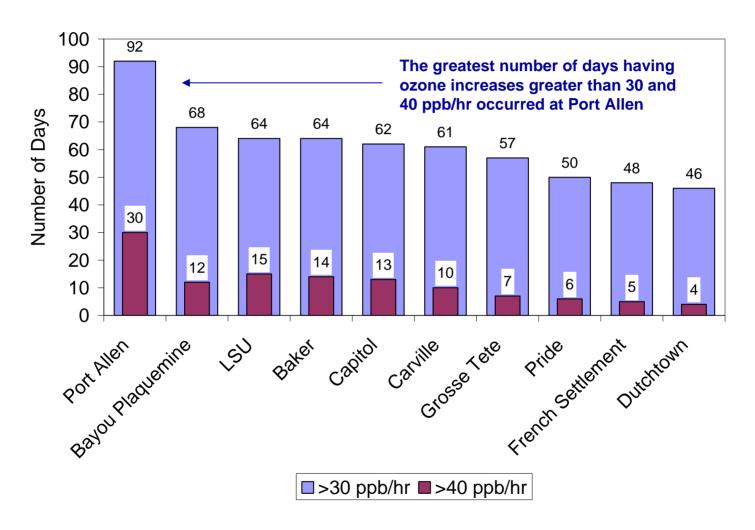


Long-Term Trend





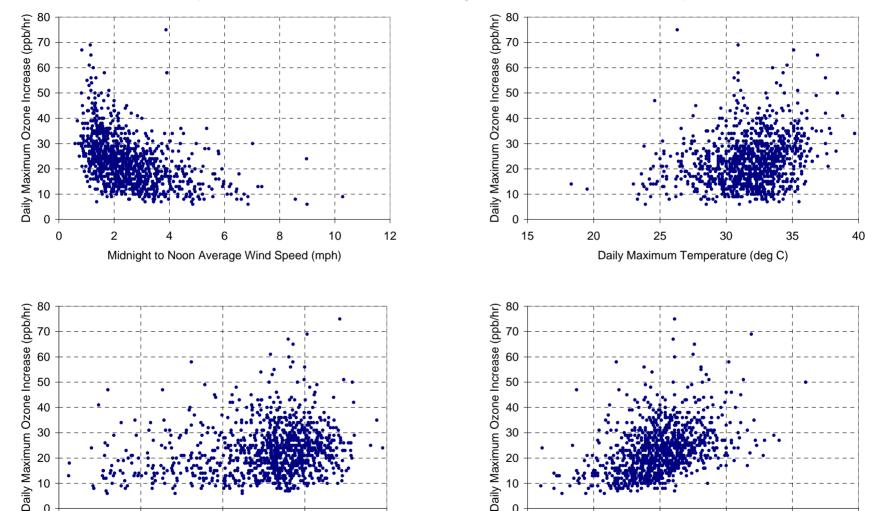
Geographical Variations





Relationship to Weather Variables

(Ozone Season Days 1997 - 2004)

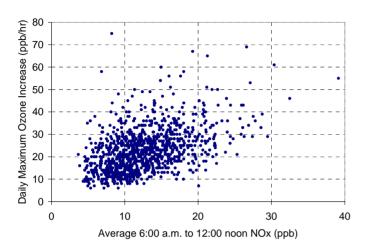


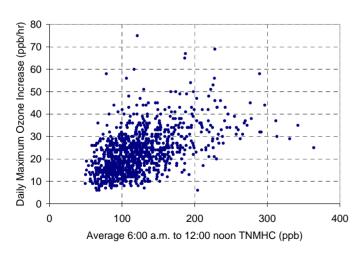
Average Hourly Solar Radiation (W/m2)

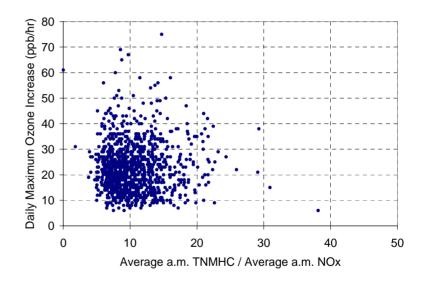
Daily Temperature Range (deg C)

Relationships to TNMHC and NOx

(Ozone Season Days 1997 - 2004)







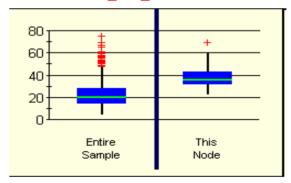


Multivariate Analysis Using Classification and Regression Tree (CART)

- CART is a statistical technique used to partition data in similar groups based on numerical or categorical variables
- Produces decision trees based on simple yes/no questions to reveal patterns in the data
- Results show that day-to-day differences in daily maximum hourly ozone increase are attributed most to:
 - a.m. TNMHC max
 - a.m. wind speed average
 - a.m. NOx max
 - daily temperature range

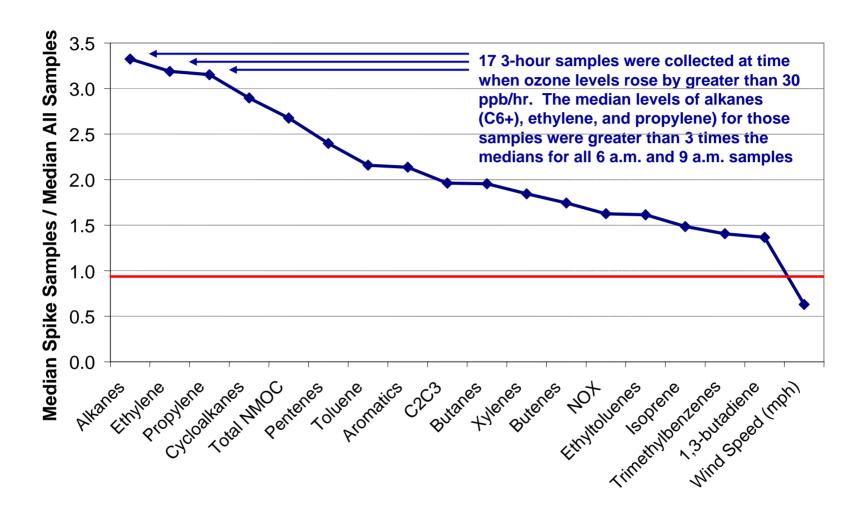
CART Terminal Node 4

AM_WS <= 2.05 & RANGE_T > 11.85 & TNMHC AM MAX > 506



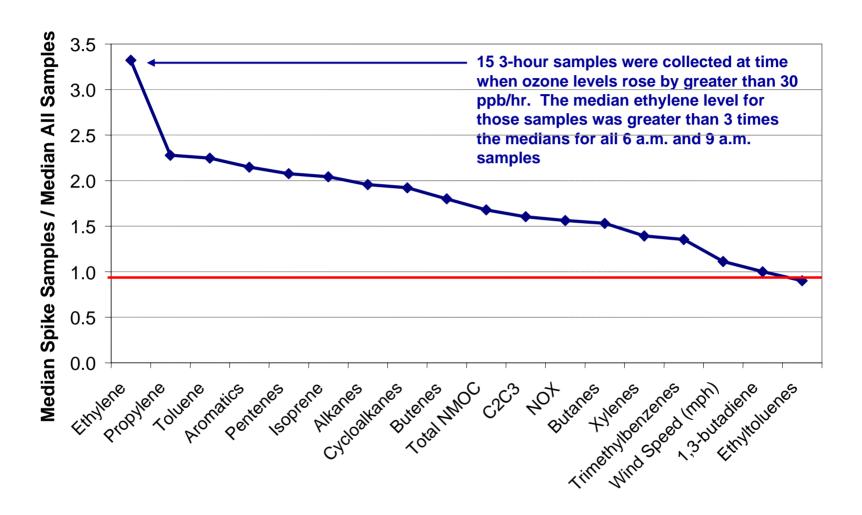


VOC levels during Sudden Ozone Increases (>30 ppb/hr) Compared with All data (6 – 11 AM): Capitol Site





VOC levels during Sudden Ozone Increases (>30 ppb/hr) Compared with All data (6 – 11 AM): Bayou Plaquemine





Summary of Ozone Spike Analysis (page 1 of 3)

- Ozone concentration increases > 40 ppb/hr occurred on 5% of ozone season days 1997 – 2004
- Ozone concentration increases > 30 ppb/hr occurred on 18% of ozone season days 1997 -2004
- Approximately 50% of 1-hour ozone exceedance days had ozone concentration increases > 40 ppb/hr; almost all had ozone concentration increases > 30 ppb/hr
- Approximately 25% of 8-hour ozone exceedance days had ozone concentration increases > 40 ppb/hr; almost all had ozone concentration increases > 20 ppb/hr



Summary of Ozone Spike Analysis (page 2 of 3)

- Maximum frequency of occurrence was 8:00 to 10:00 a.m. CST
- Maximum frequency of occurrence was on Fridays and Saturdays
- Maximum frequency of occurrence was July October, with secondary peak during April – June
- Fewer occurrences during 2001-2004 than during 1997-2000
- Frequency of occurrence was greatest at Port Allen; least at outlying monitoring sites



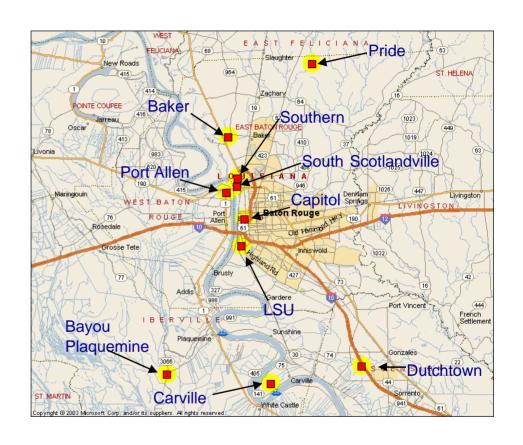
Summary of Ozone Spike Analysis (page 3 of 3)

- Sudden ozone concentration increases appeared to be related to wind speed (inversely) more than any other measured meteorological variable
- Sudden ozone concentration increases appeared to be related to the morning levels of both TNMHC and NOx but not the average TNMHC/NOx ratio
- 3-hour canister samples collected the Capitol and Bayou Plaquemine site at times when ozone levels increased by greater than 30 ppb/hr had greater than average levels of ethylene, propylene, other VOC, and NOx



Analysis of VOC Reactivity

- 10 monitoring sites
- Data from 1998 –
 September 2004
- 24-hour samples for all sites
- 24-hour and 3-hour samples for:
 - Bayou Plaquemine
 - Capitol
 - Pride
- Did not use strike samples for reactivity assessment – only routine samples





TNMOC and Total MIR Summary

(from 24-Hour Canisters)

	TNMOC (ppb-C)		MIR		
Site	Mean	Median	Mean	Median	Period of Record
Port Allen	517	339	228	171	Setpember '03 - October '04
South Scotlandville	264	220	205	164	May '99 - October '04
Southern	273	175	195	131	May '99 - October '04
LSU	218	195	119	116	August '03 - October '04
Capitol	224	193	145	120	January '98 - October '04
Baker	171	150	117	82	July '02 - October '04
Carville	125	116	74	68	May '04 - October '04
Dutchtown	117	103	80	73	January '99 - October '04
Bayou Plaquemine	114	101	72	63	January '98 - October '04
Pride	91	70	74	68	January '98 - October '04

- TNMOC and reactivity (MIR) average levels were highest at Port Allen but data record at Port Allen is only ~1 year long (09/03 – 10/04)
- In general, sites in central Baton Rouge (Port Allen, South Scotlandville, Southern, LSU, and Capitol) had higher TNMOC and reactivity levels than the outlying sites (Baker, Carville Dutchtown, Bayou Plaquemine, and Pride)



Spatial Distribution of Median VOC Reactivity

Median MIR by Latitude & Longitude

163.8 to 180.0

147.5 to 163.7

131.3 to 147.4

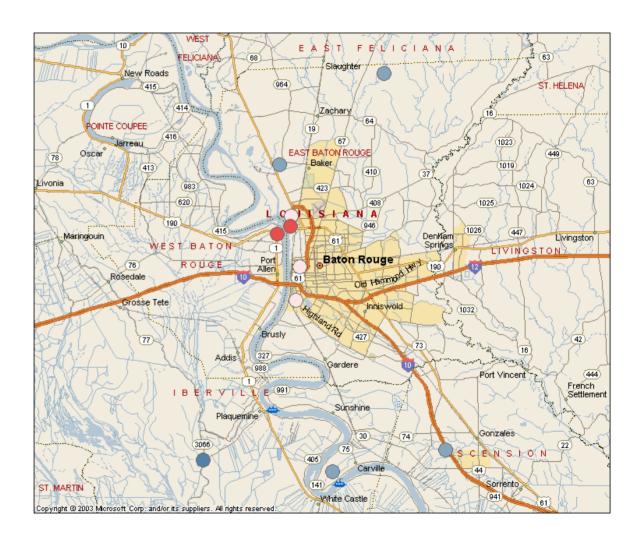
115.0 to 131.2

98.8 to 114.9

82.5 to 98.7

66.3 to 82.4

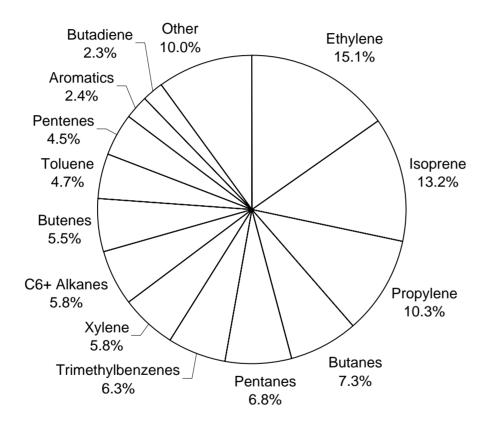
50.0 to 66.2





Reactivity Apportionment by Chemical Group

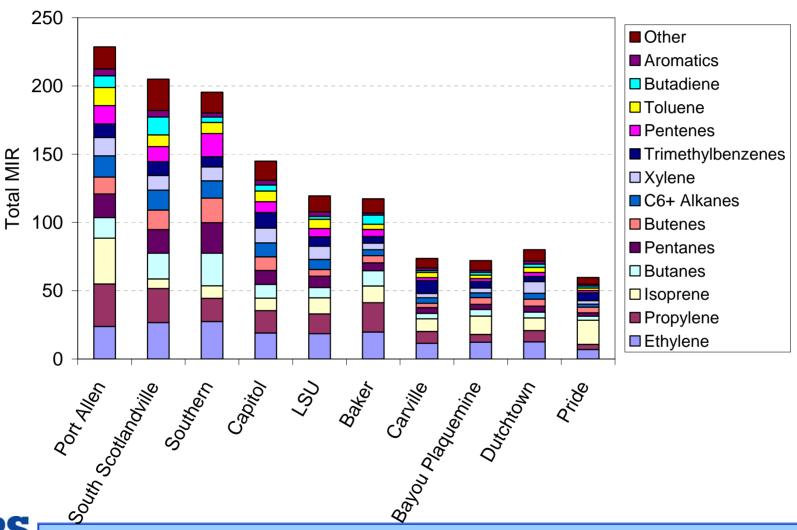
(Averaged for All Sites for 24-Hour Canisters)



Ethylene, Isoprene, and propylene comprised almost 40% of the total reactivity (on average) but no small group of compounds or chemical classes dominated overall reactivity

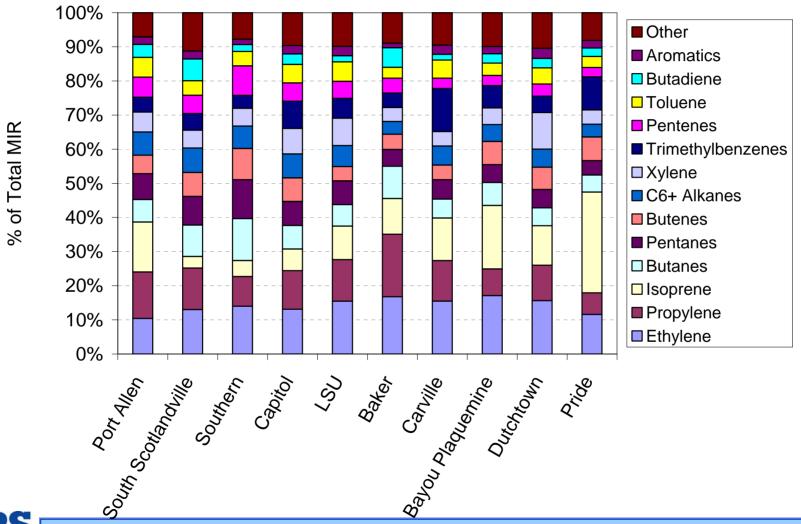


Spatial Variation in Reactivity by Chemical Group (24-Hour Canisters)





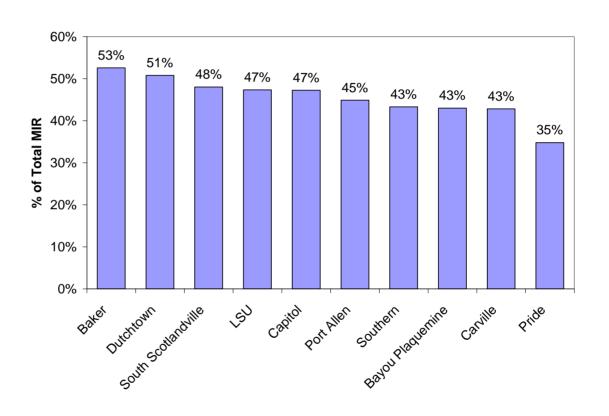
Spatial Variation in Relative VOC Reactivity Apportionment (24-Hour Canisters)





% of Total MIR Attributed to HRVOC

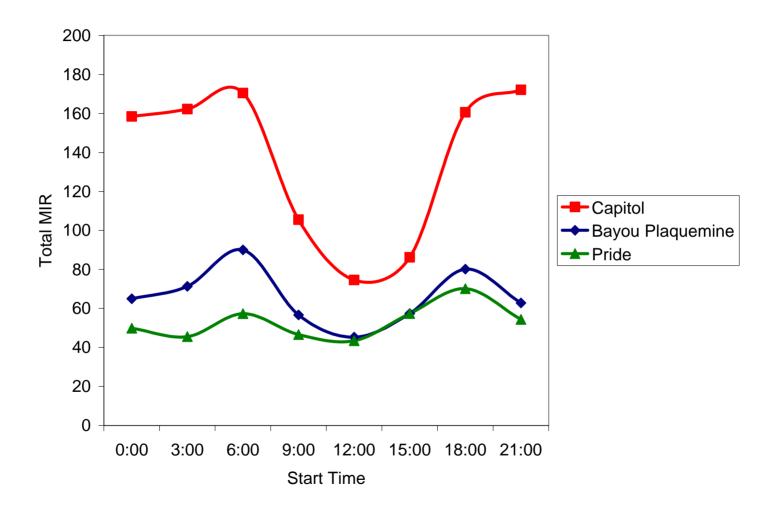
 HRVOC (i.e., ethylene, propylene, isomers of butene, 1,3-butadiene, toluene, and xylene) accounted for 35% to 53% of the total MIR, on average, at Baton Rouge sampling sites





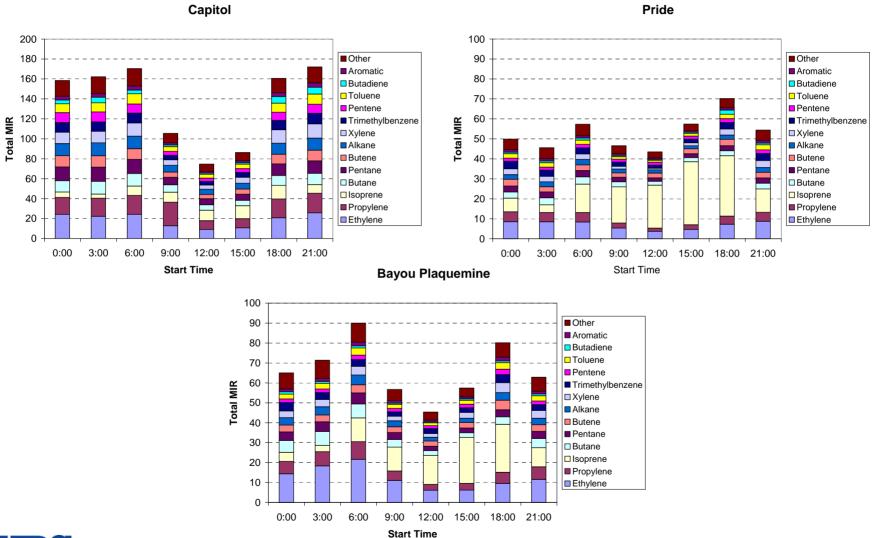
Average Diurnal Variation of VOC Reactivity

(from 3-Hour Canisters)



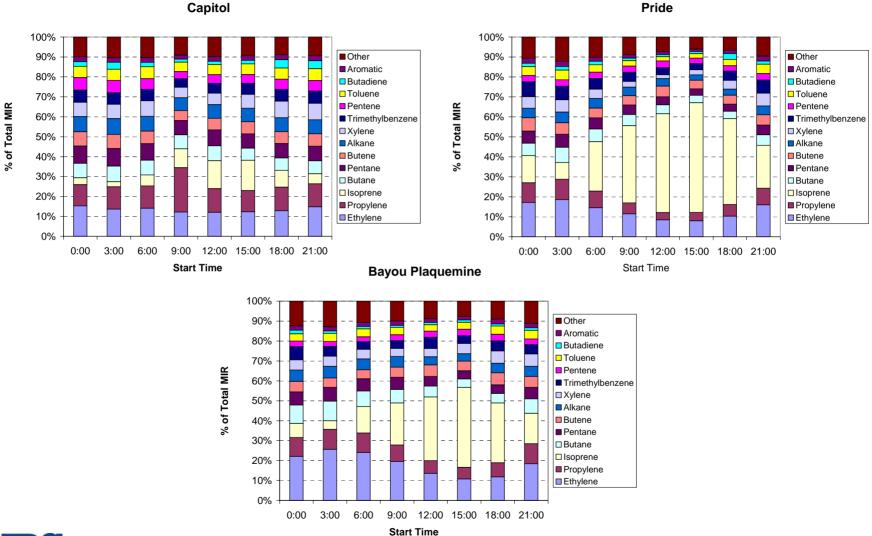


Reactivity Apportionment by Chemical Group – Diurnal Variation



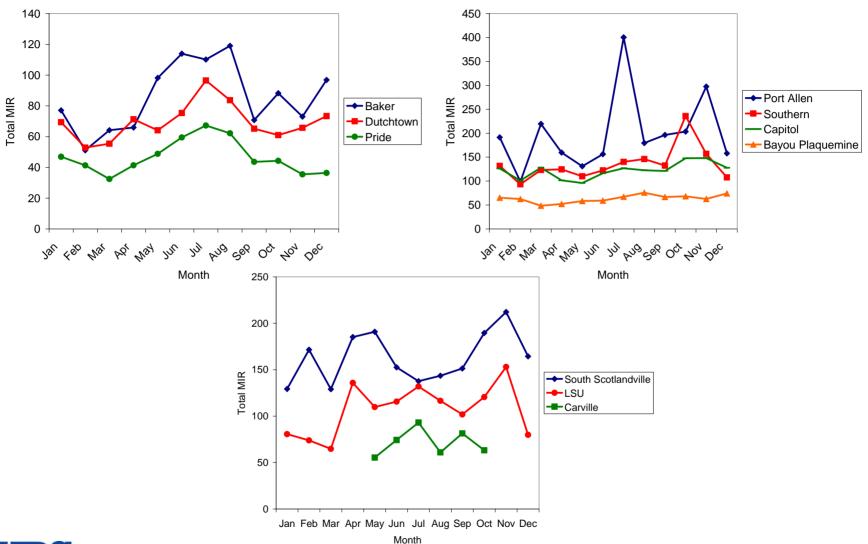


Reactivity Apportionment by Chemical Group – Diurnal Variation



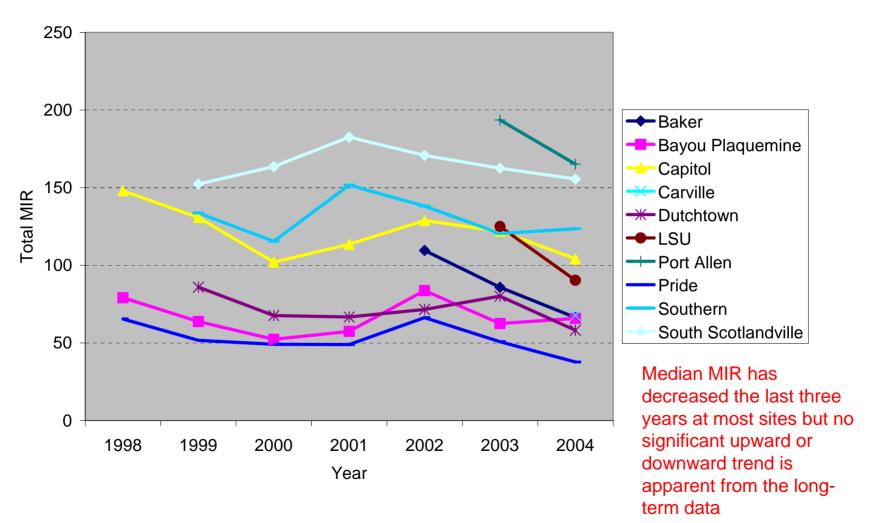


Median MIR by Month



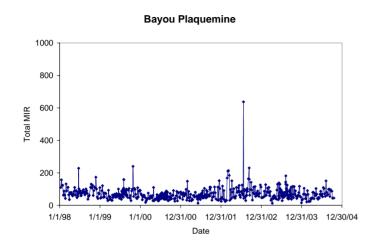


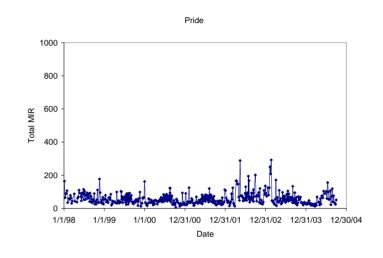
Long-Term Trend in Annual Median MIR

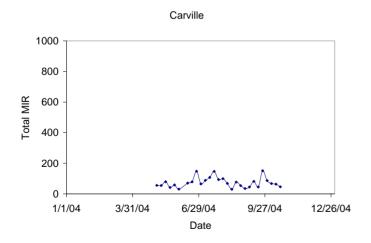


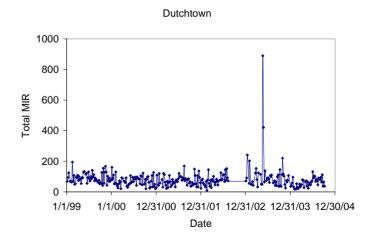


Time Series of MIR 24-Hour Values



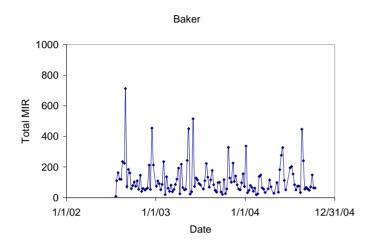


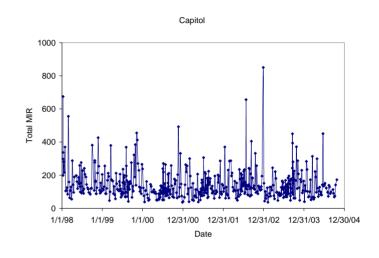


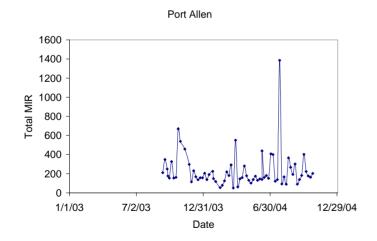


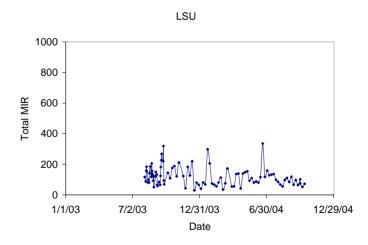


Time Series of MIR 24-Hour Values



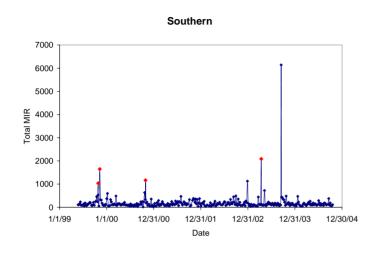


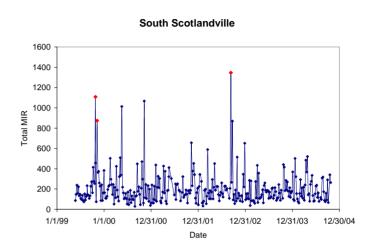






Time Series of MIR 24-Hour Values





 Day-to-day variations at all sites are greater than annual and seasonal patterns



VOC Canister Samples on Ozone Spike Days

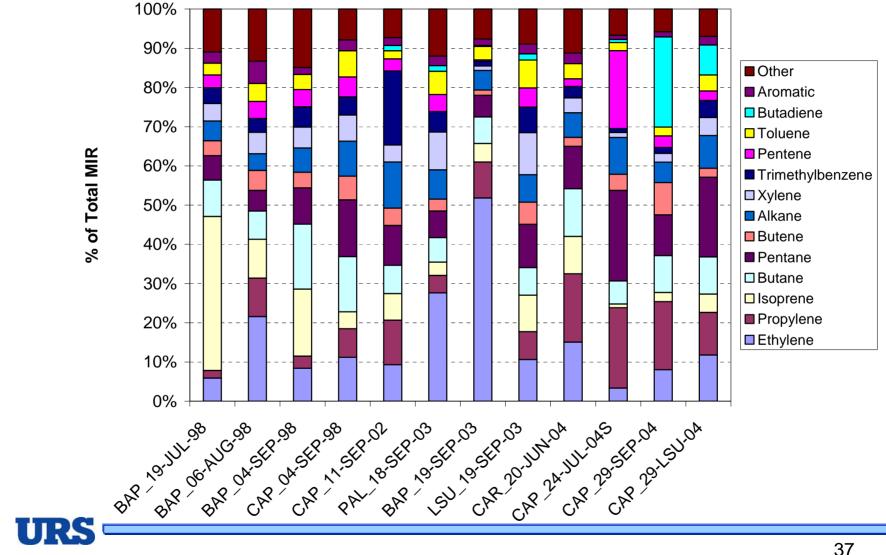
- 13 times during
 1998 2004 when
 ozone rose by
 greater than 40
 ppb/hr a canister
 was collected at the
 site measuring the
 rapid ozone rise
- VOC were sampled during ozone spike events 9 times with 3-hour canisters, 3 times with 24-hour canisters, and once with a 25-minute triggered canister

					Median MIR
		START		Total MIR for	for Site and
COLDATE	LOCCODE	HOUR	DURATION	Sample	Time of Day
7/19/98	CAN_BAP	6	3	104	90
8/6/98	CAN_BAP	9	3	66	56
9/4/1998	CAN_BAP	6	3	98	90
9/4/1998	CAN_CAP	9	3	577	106
9/11/02	CAN_CAP	0	24	405	120
9/18/03	CAN_PAL	0	24	349	171
9/19/03	CAN_BAP	9	3	234	106
9/19/03	CAN_LSU	0	24	267	116
6/20/04	CAN_CARV	9	3	122	68
7/24/04	CAN_CAP	7	0.42	2248	170
7/24/04	CAN_CAP	6	3	864	170
9/29/04	CAN_CAP	9	3	644	106
9/29/04	CAN_LSU	9	3	203	116

Some samples appear ordinary while others had much higher than normal reactivity



VOC Speciated Contributions to Total Reactivity during Ozone Spikes



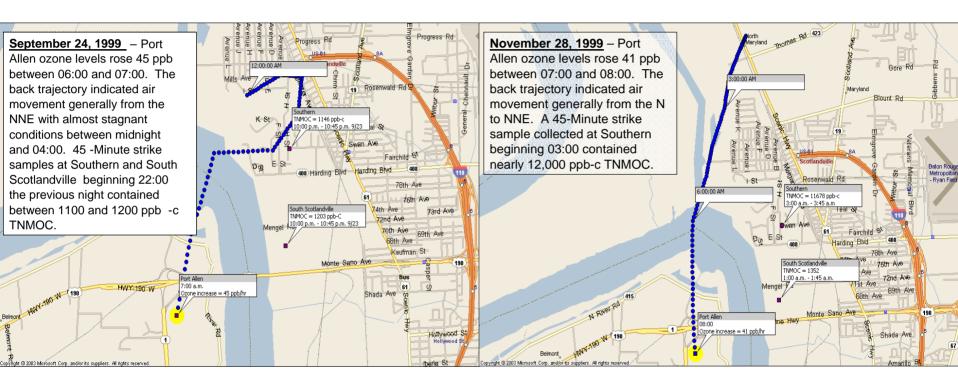


Back Trajectory Analysis

- No cases where a canister sample was collected directly on the trajectory path back from a site where a sudden ozone increase (> 40 ppb/hr) was measured
- Several cases where canister samples were collected in the general upwind direction, assuming a wide margin of uncertainty in the trajectory path
- Most canister samples that were collected roughly upwind of where a sudden ozone increase was measured had higher than average TNMOC levels, with several (10 of 22) having TNMOC levels greater than 1 ppm



Back Trajectory Examples





Summary for VOC Samples Collected Roughly Upwind of Rapid Ozone Increases

SAMPNO	COLDATE	LOCCODE	START_HOUR	DURATION	Total NMOC
AA02738	8/27/1998	Capitol	6	3	324.615
AA02754	8/29/1998	Capitol	0	3	354.654
AA03166	10/2/1998	Capitol	6	3	1149.278
AB02935	8/7/99	Capitol	6	3	333.45
AB03705	9/23/99	Southern	22	.75	1146.23
AB03703	9/23/99	South Scotlandville	22	.75	1203.09
AB04418	11/28/99	Southern	3	.75	11673.10
AB04420	11/28/99	South Scotlandville	1	.75	1352.20
AC01529	5/16/00	Southern	0	.75	7994.70
AC02360	7/2/00	Capitol	6	3	303.40
AC03641	8/25/00	Capitol	6	3	625.40
AC03581	8/25/00	South Scotlandville	3	.75	228.80
AC03820	9/3/00	Capitol	9	3	279.70
AC04358	10/15/00		6	3	274.60
AC04521	10/27/00	South Scotlandville	0	24	663.10
AC04519	10/27/00	Southern	0	24	612.40
AC04516	10/28/00	Southern	0	24	1056.30
AC04996	12/9/00	Southern	1	0.75	1560.60
AD23488		Dutchtown	0	24	100.00
AD26943	11/6/01	South Scotlandville	23	.75	1121.00
AD27752	11/18/01	Southern	6	.75	8264.00
AE14022	7/1/02	Capitol	6	3	150.00
AE18382	8/21/02	Capitol	6	3	545.00
AF07095	4/14/03	Southern	5	24	2392.00
AF20969	9/18/03	South Scotlandville	0	24	333.00
AF20971	9/19/03	Southern	6	.75	4923.00



VOC Reactivity Summary Page 1 of 4

- Greater ozone-forming potential, in terms of median MIR, was measured at sampling sites closer to central Baton Rouge than at outlying sampling sites
- Ethylene, isoprene, and propylene were the greatest individual contributors to the total MIR, averaged across all sampling sites; together these compounds comprised close to 40% of the total
- The next greatest contributors, on an individual compound basis, were toluene, isopentane, n-butane, m/p-xylene, and 1,2,4-trimethylbenzene
- HRVOC accounted for 43% to 53% of the total MIR at all the Baton Rouge sampling sites except Pride (where HRVOC was 35% of the total)
- Isoprene had the greatest variability between different monitoring sites; in terms of its contribution to total reactivity isoprene ranged from 3% at South Scotlandville to 30% at Pride



VOC Reactivity Summary Page 2 of 4

- Total reactivity-weighted VOC concentrations were greatest during the 6:00 – 9:00 a.m. and 6:00 p.m. – 9:00 p.m. sampling periods and least during the 12:00 noon – 3:00 p.m. sampling period at sites where 3-hour samples were routinely collected
- The average diurnal variation in total reactivity-VOC level was about a factor of two
- The isoprene impact was greatest during mid-late afternoon, on average, while non-isoprene VOC were most important during the morning
- Isoprene made up about 50% of the total reactivity during midlate afternoon at the Pride sampling site (where the nonisoprene VOC contribution was least in relative and absolute terms)



VOC Reactivity Summary Page 3 of 4

- Ozone-forming potential at the Baker, Pride, and Dutchtown monitors was greater during summer than at other times of the year and this pattern appears to be caused by the isoprene seasonal cycle
- Median MIR levels decreased over the past three years at most sites but no significant upward or downward trend is apparent from the longer term data
- Day-to-day variations in ozone-forming potential appear to be greater than any long-term or seasonal trends



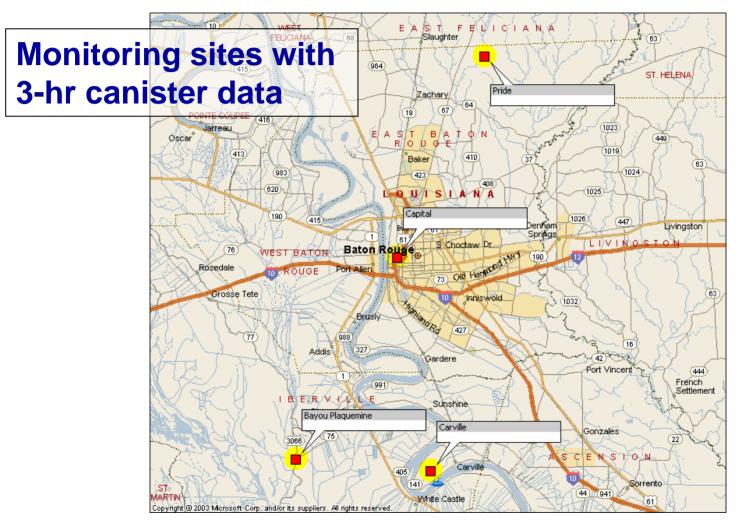
VOC Reactivity Summary

Page 4 of 4

- 13 canister samples were collected at times and places where ozone levels rose more than 40 ppb/hr; the total MIR for most of those samples were greater than for the average of samples collected at the same monitoring site and time of day
- Trajectories projected back in time from a site of a sudden ozone increase (> 40 ppb/hr) passed "near" a monitoring site where a VOC sample was collected on 22 occasions; most of the 22 VOC samples had higher than average TNMOC levels (10 had TNMOC levels > 1 ppm)



Comparing Monitored Levels of HRVOC and NOx with the Emissions Inventory





Emissions Inventory Evaluation Overview

- Compare ratios of speciated HRVOC to NOx measured for discrete wind direction bins with ratios of estimated upwind emissions
- Large discrepancies between the monitored ratios and the estimated emissions ratios suggest errors in the estimated emissions
- TCEQ found HRVOC/NOx in ambient air frequently about an order of magnitude greater than the HRVOC/NOx ratio of estimated upwind emissions



Emissions Inventory Evaluation Assumptions and Limitations

- Ambient monitoring data are influenced only by fresh emissions
- Influence of point source emissions can be isolated from mobile and area source influences
- HRVOC and NOx emissions are homogeneously mixed by the time the emissions reach the monitoring site
- No chemical losses due to reactions or deposition
- Measurement errors are insignificant



Emissions Inventory Evaluation Approach

Emissions Data

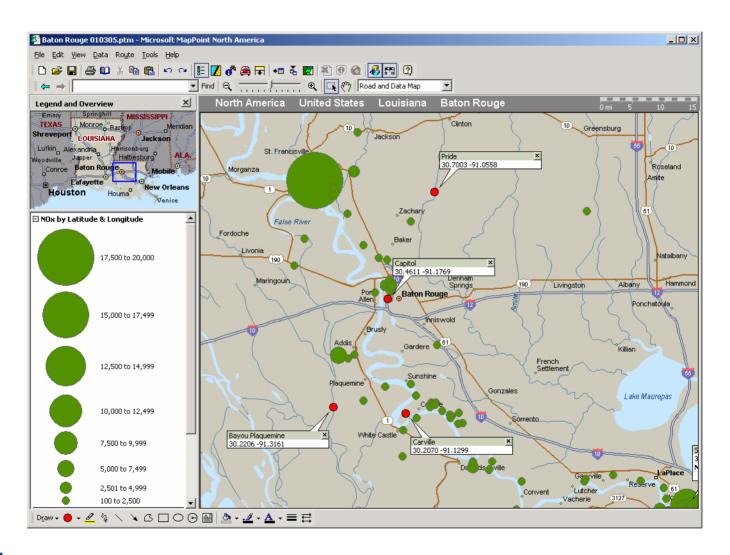
- Used 2003 HRVOC emissions inventory provided by LDEQ
- Separated emissions into 10-degree directional bins centered on each monitoring site
- Weighted emissions 1/distance from monitoring site
- Smoothed directional differences using cosine function to simulate dispersion

Monitoring Data

- Used 3-hour canister data from 2002-2004
- Used only samples starting at 00:00, 03:00, 06:00 and 21:00
- Filtered out samples with wind speed less than 2 mph
- Separated data into 10-degree wind sectors

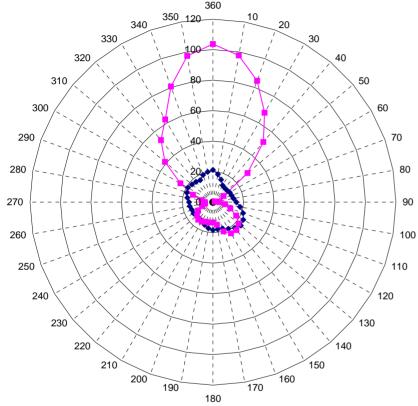


NOx Point Sources

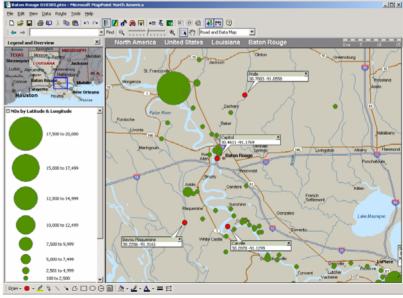




Capitol NOx Measurements and Distance-Weighted Emissions

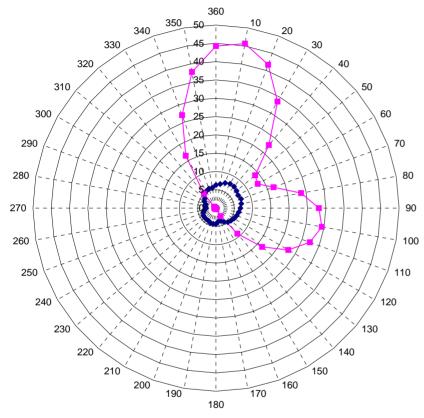


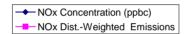


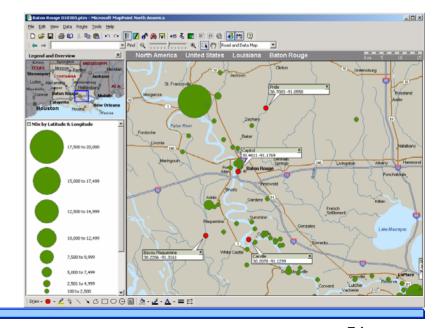




Bayou Plaquemine NOx Measurements and Distance-Weighted Emissions

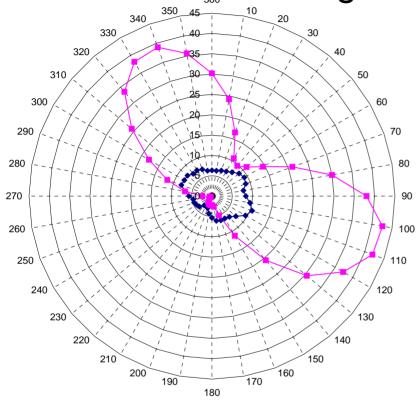




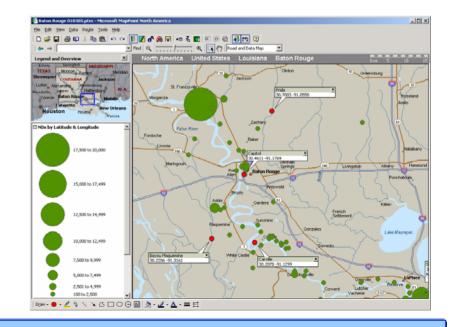




Carville NOx Measurements and Distance-Weighted Emissions

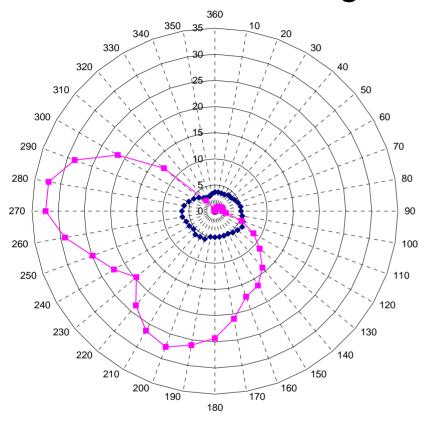


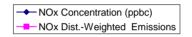
NOx Concentration (ppbc)
NOx Dist.-Weighted Emissions

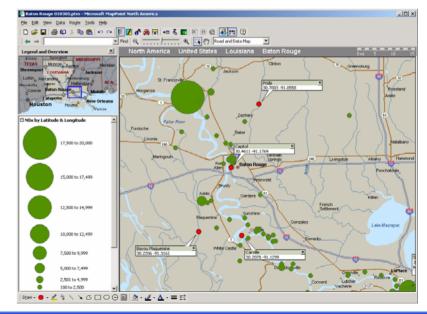




Pride NOx Measurements and Distance-Weighted Emissions

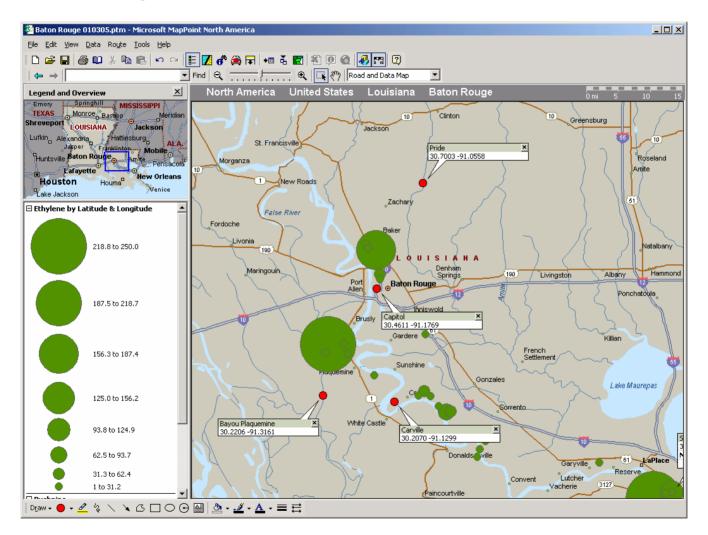






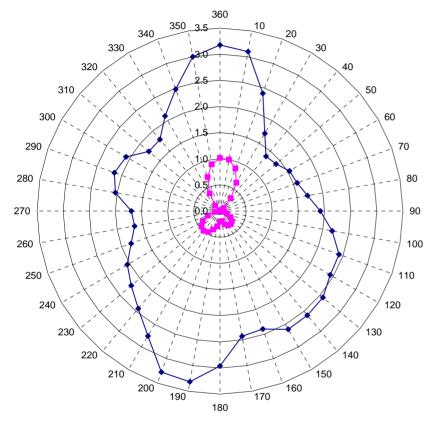


Ethylene Point Sources



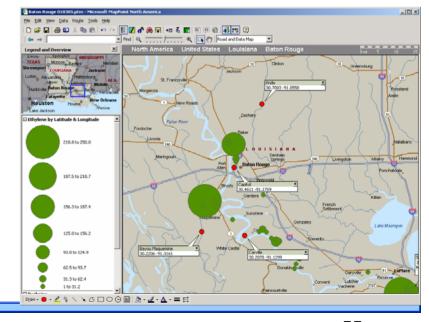


Capitol Ethylene Measurements and Distance-Weighted Emissions



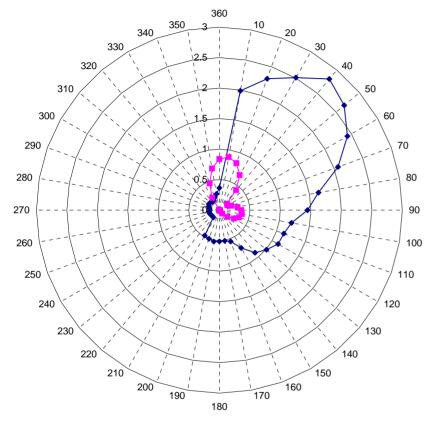
Ethylene Concentration (ppbc)

Ethylene Dist.-Weighted Emissions

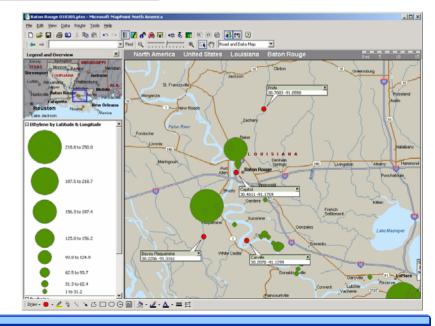




Bayou Plaquemine Ethylene Measurements and Distance-Weighted Emissions

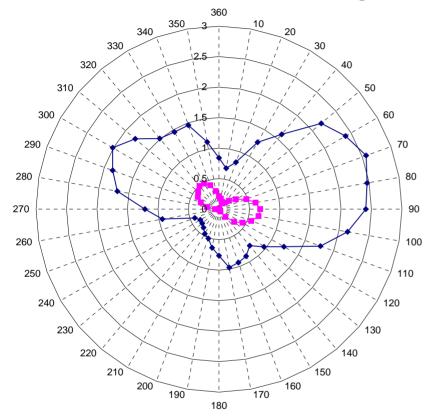






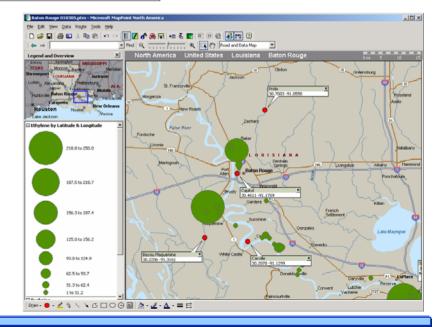


Carville Ethylene Measurements and Distance-Weighted Emissions



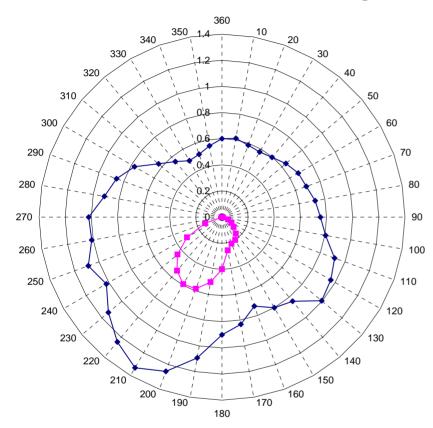
Ethylene Concentration (ppbc)

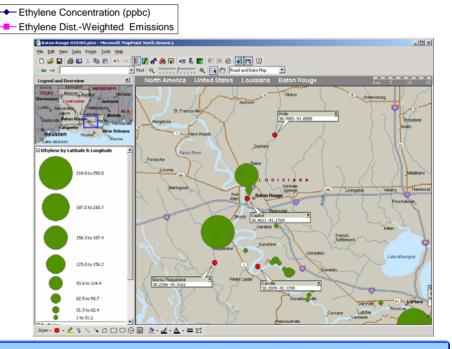
Ethylene Dist.-Weighted Emissions





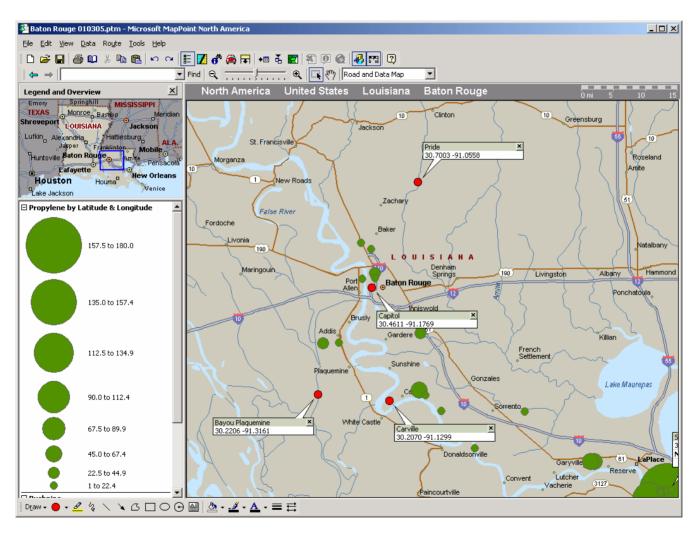
Pride Ethylene Measurements and Distance-Weighted Emissions





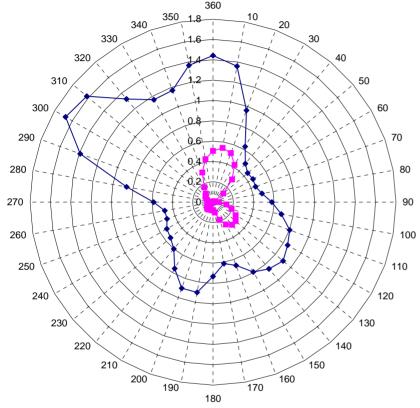


Propylene Point Sources

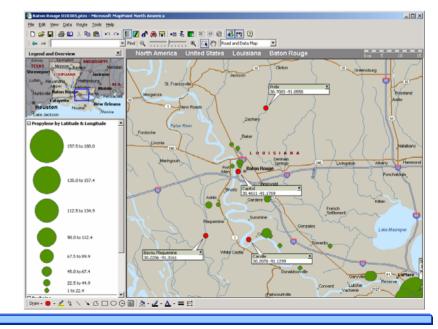




Capitol Propylene Measurements and Distance-Weighted Emissions

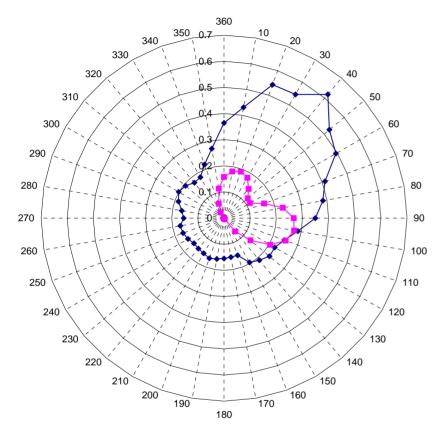


Propylene Concentration (ppbc)
Propylene Dist.-Weighted Emissions

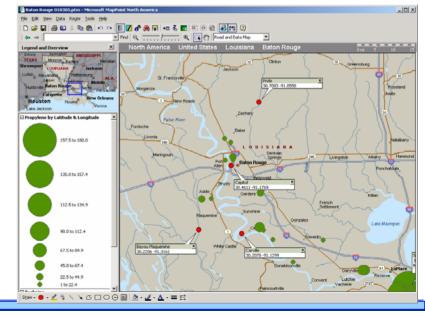




Bayou Plaquemine Propylene Measurements and Distance-Weighted Emissions

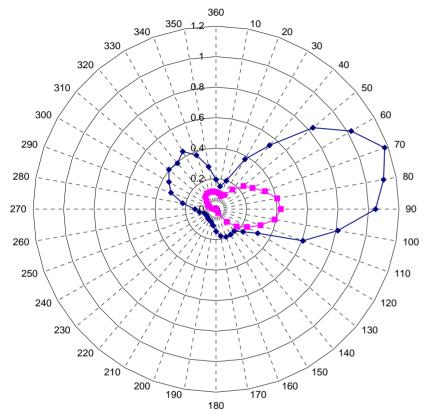


Propylene Concentration (ppbc)
Propylene Dist.-Weighted Emissions

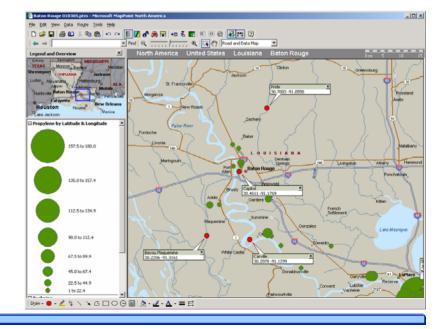




Carville Propylene Measurements and Distance-Weighted Emissions

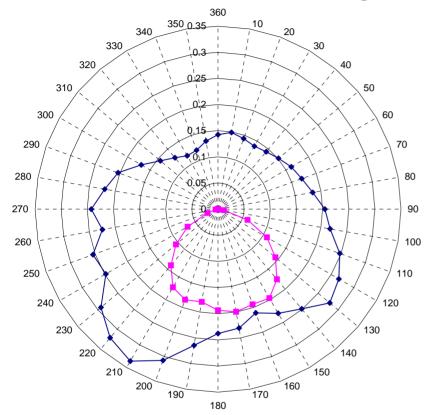


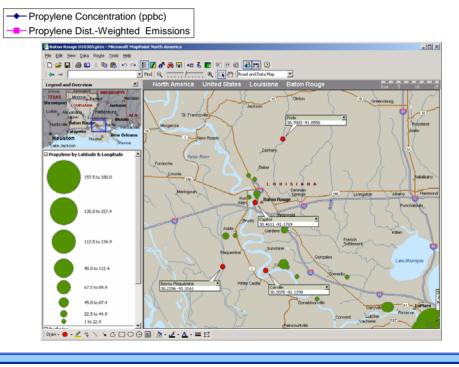
Propylene Concentration (ppbc)
Propylene Dist.-Weighted Emissions





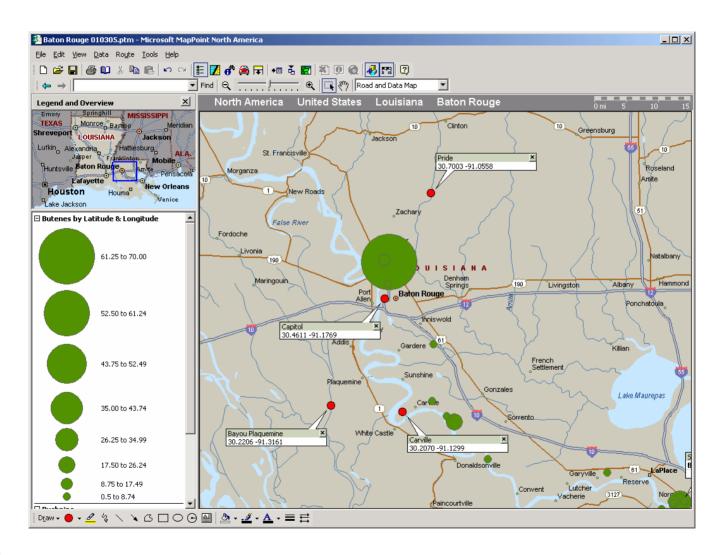
Pride Propylene Measurements and Distance-Weighted Emissions





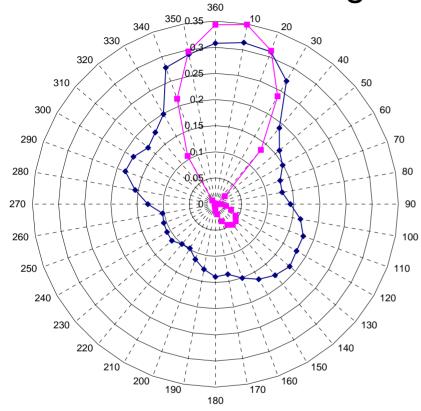


Butene Point Sources



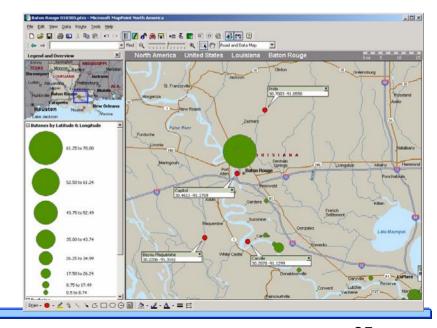


Capitol Butene Measurements and Distance-Weighted Emissions



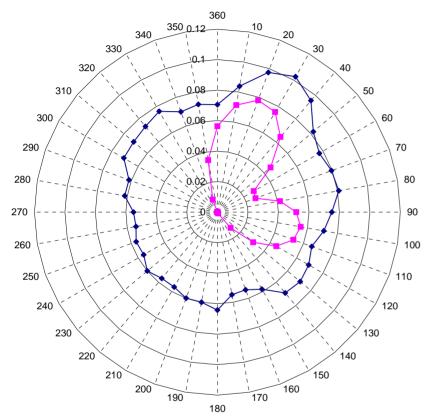
→ 1-Butene Concentration (ppbc)

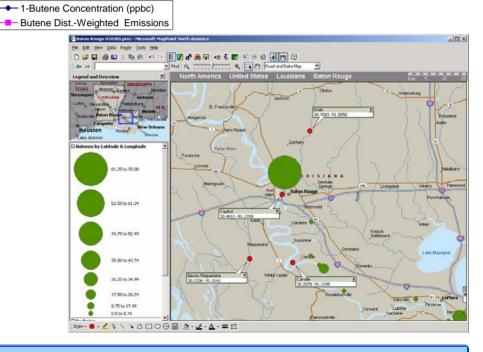
— Butene Dist.-Weighted Emissions





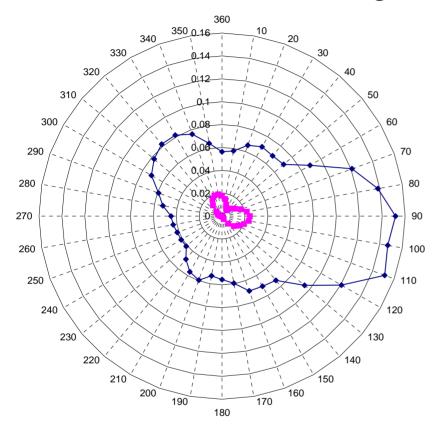
Bayou Plaquemine Butene Measurements and Distance-Weighted Emissions

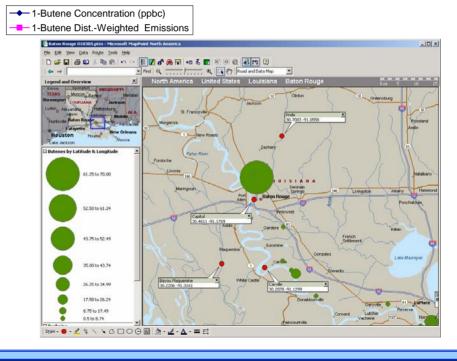






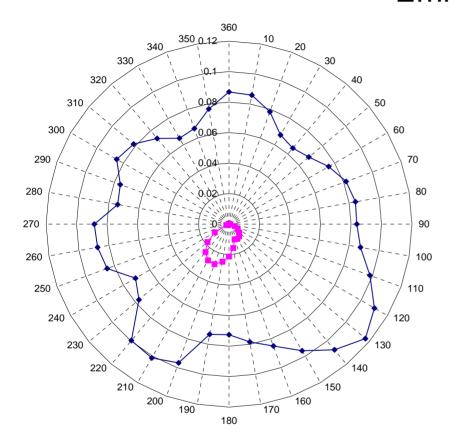
Carville 1-Butene Measurements and Distance-Weighted Emissions

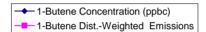


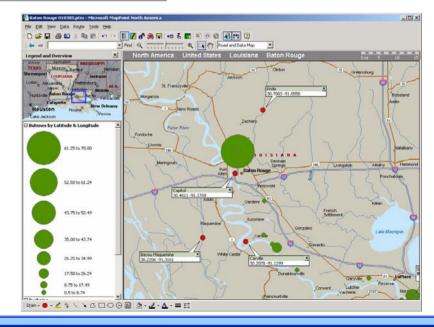




Pride 1-Butene Measurements and Distance-Weighted Emissions

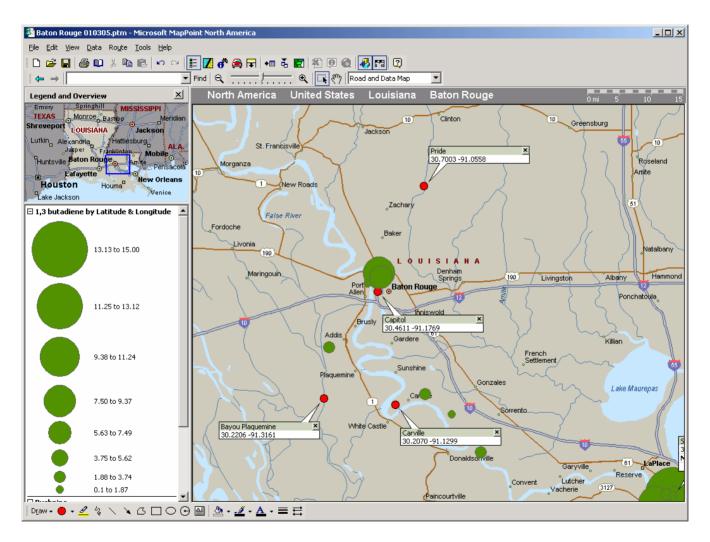






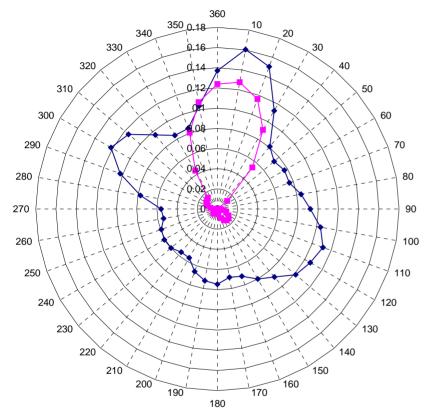


1,3-Butadiene Point Sources

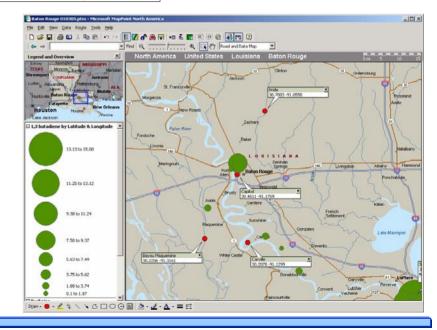




Capitol 1,3-Butadiene Measurements and Distance-Weighted Emissions

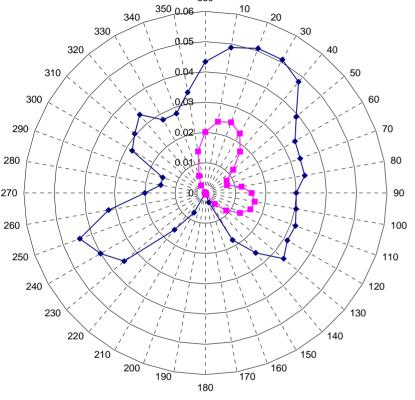


1,3-Butadiene Concentration (ppbc)
1,3-Butadiene Dist.-Weighted Emissions



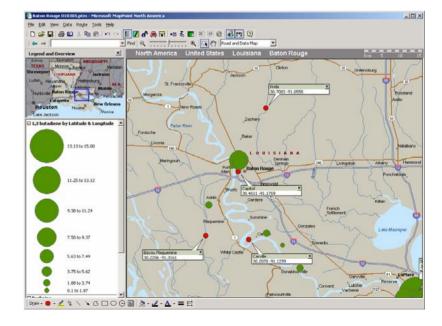


Bayou Plaquemine 1,3-Butadiene Measurements and Distance-Weighted Emissions



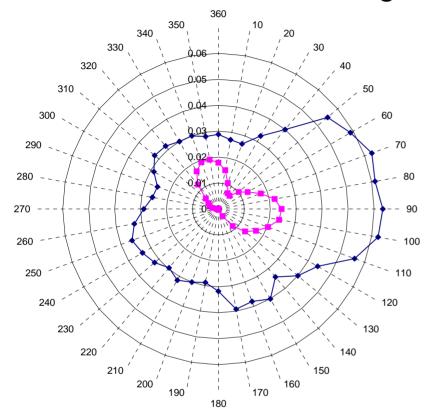
→ 1,3-Butadiene Concentration (ppbc)

1,3-Butadiene Dist.-Weighted Emissions



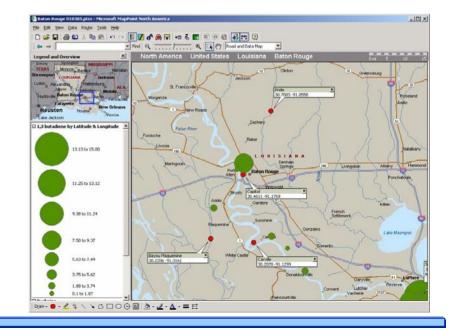


Carville 1,3-Butadiene Measurements and Distance-Weighted Emissions



→ 1,3-Butadiene Concentration (ppbc)

1,3-Butadiene Dist.-Weighted Emissions





Pride 1,3-Butadiene Measurements and Distance-Weighted Emissions

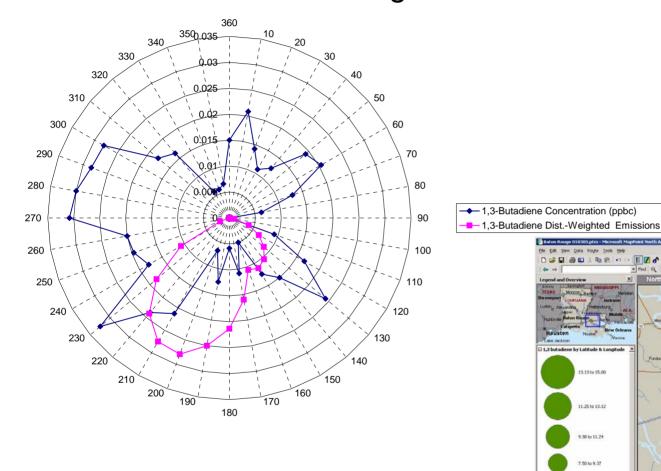
13.13 to 15.00

11.25 to 13.12

9.38 to 11.24

5.63 to 7.49 3.75 to 5.62 1.88 to 3.74

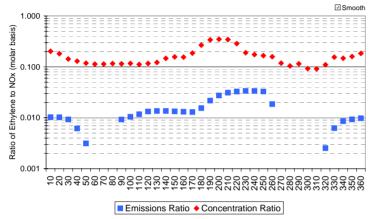
DEW- - - 2 4 \ \ G□○⊕ ■ 2 - 2 - 4 - = #



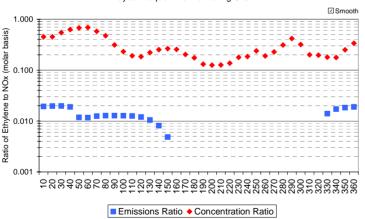


Average Monitored and Emitted Ethylene/NOx Ratios

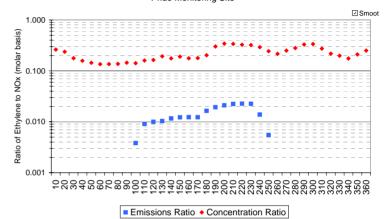
Average Ethylene Conc. / Average NOx Conc. by Wind Direction and Ethylene Emissions / NOx Emissions by Compass Direction at Capitol Monitoring Site



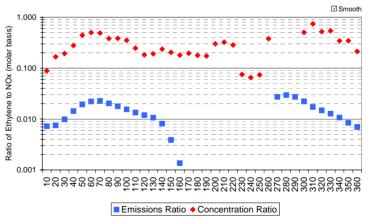
Average Ethylene Conc. / Average NOx Conc. by Wind Direction and Ethylene Emissions / NOx Emissions by Compass Direction at Bayou Plaquemine Monitoring Site



Average Ethylene Conc. / Average NOx Conc. by Wind Direction and Ethylene Emissions / NOx Emissions by Compass Direction at Pride Monitoring Site



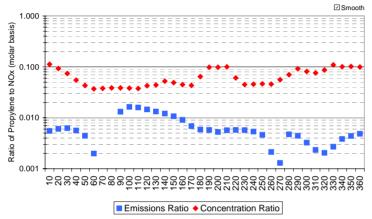
Average Ethylene Conc. / Average NOx Conc. by Wind Direction and Ethylene Emissions / NOx Emissions by Compass Direction at Carville Monitoring Site



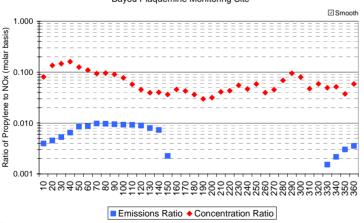


Average Monitored and Emitted Propylene/NOx Ratios

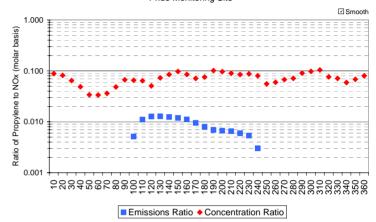
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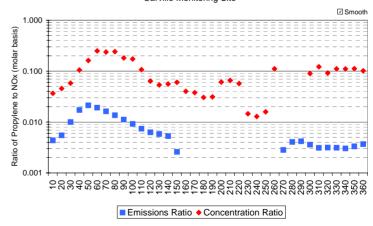
Average Propylene Conc. / Average NOx Conc. by Wind Direction and Propylene Emissions / NOx Emissions by Compass Direction at Bayou Plaquemine Monitoring Site



Average Propylene Conc. / Average NOx Conc. by Wind Direction and Propylene Emissions / NOx Emissions by Compass Direction at Pride Monitoring Site



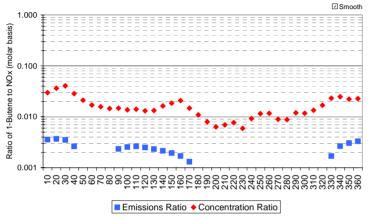
Average Propylene Conc. / Average NOx Conc. by Wind Direction and Propylene Emissions / NOx Emissions by Compass Direction at Carville Monitoring Site



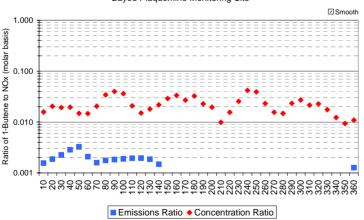


Average Monitored and Emitted Butene/NOx Ratios

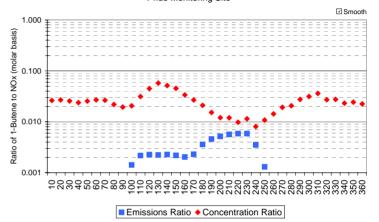
Average 1-Butene Conc. / Average NOx Conc. by Wind Direction and Butenes Emissions / NOx Emissions by Compass Direction at Capitol Monitoring Site



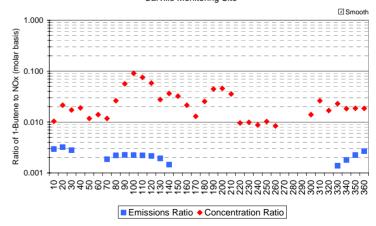
Average 1-Butene Conc. / Average NOx Conc. by Wind Direction and Butenes Emissions / NOx Emissions by Compass Direction at Bayou Plaquemine Monitoring Site



Average 1-Butene Conc. / Average NOx Conc. by Wind Direction and Butenes Emissions / NOx Emissions by Compass Direction at Pride Monitoring Site



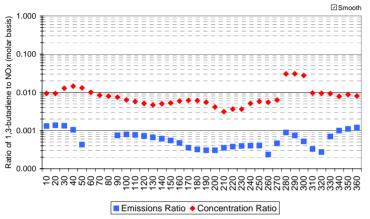
Average 1-Butene Conc. / Average NOx Conc. by Wind Direction and Butenes Emissions / NOx Emissions by Compass Direction at Carville Monitoring Site



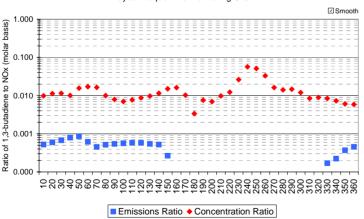


Average Monitored and Emitted 1,3-Butadiene/NOx Ratios

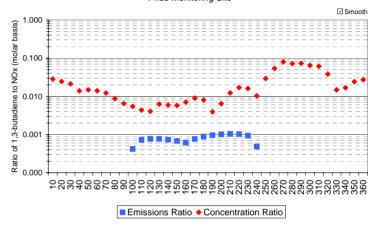
Average 1,3-butadiene Conc. / Average NOx Conc. by Wind Direction and 1,3 butadiene Emissions / NOx Emissions by Compass Direction at Capitol Monitoring Site



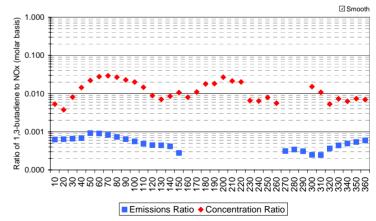
Average 1,3-butadiene Conc. / Average NOx Conc. by Wind Direction and 1,3 butadiene Emissions / NOx Emissions by Compass Direction at Bayou Plaquemine Monitoring Site



Average 1,3-butadiene Conc. / Average NOx Conc. by Wind Direction and 1,3 butadiene Emissions / NOx Emissions by Compass Direction at Pride Monitoring Site



Average 1,3-butadiene Conc. / Average NOx Conc. by Wind Direction and 1,3 butadiene Emissions / NOx Emissions by Compass Direction at Carville Monitoring Site





Average HRVOC and NOx Levels and in ppb-v and HRVOC/NOx Ratios

Average Le	evel in ppb-v f	or 21:0	0 - 08:00	, January	2002	2 - Septembe	er 2004
	Ethylene	Prop	ylene	Buten	es	1,3-Butadie	ne NOx
Bayou Plaquemine	3.22	0	.72	0.39		0.11	7.95
Capitol	4.33	1	.75	0.67	'	0.43	25.23
Carville	3.00	1	.03	0.40		0.11	9.19
Pride	1.38	0	.43	0.26		0.09	5.76
HRV OC/NOx Ratios							
	Ethyle	ne	Prop	ylene	E	Butenes	1,3-Butadien
Bayou Plaquemir	ne 0.40	5	0.	091		0.049	0.014
Capitol	0.17	2	0.	069		0.027	0.017
Carville	0.32	6	0.	112		0.044	0.012
Pride	0.24	0	0.	074		0.046	0.015
Emitted	0.03	2	0.	007		0.003	0.001

Ratios of regional emissions are about an order of magnitude less than the monitored ratios



Emissions Inventory Evaluation Results

- Monitored NOx and HRVOC levels show variations with wind direction that are generally consistent with locations of point sources, with a few exceptions
- Monitored HRVOC/NOx ratios are roughly an order of magnitude greater than the ratios derived from reported emissions
- This is <u>not</u> to say that actual emissions are an order of magnitude greater than reported – too much uncertainty in the analysis



VOC Source Apportionment

- Used EPA beta release of Positive Matrix Factorization (PMF)
- Applied 3-hour canister samples collected with start times between 9:00 p.m. and 6:00 a.m.
- Used 2003 and 2004 data
- Emphasis on North Baton Rouge Monitoring Sites

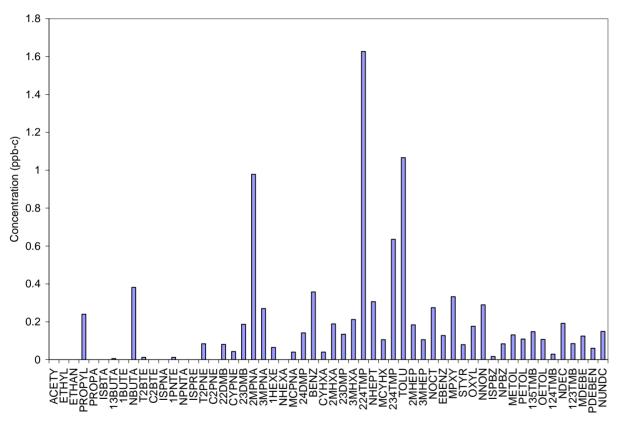


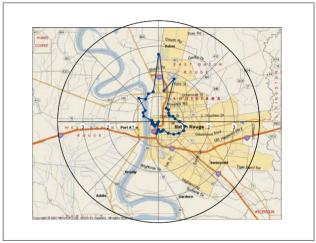
Overview of PMF

- Multivariate factor analysis tool
- Applied widely to PM2.5 data
- Also applied to VOC data
- Variable weighting of data based on analytical uncertainties
- Requires ambient monitoring data only no user assumed source profiles



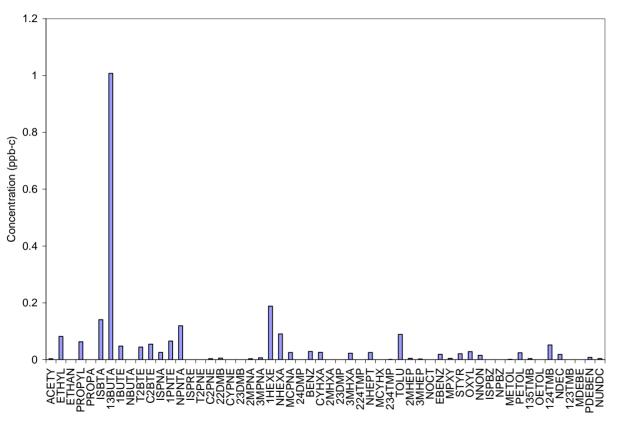
Capitol 3-Hour Source Factor 1

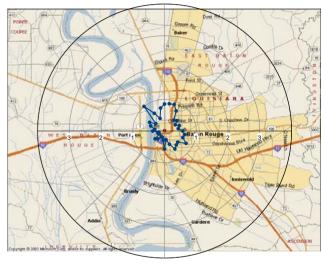




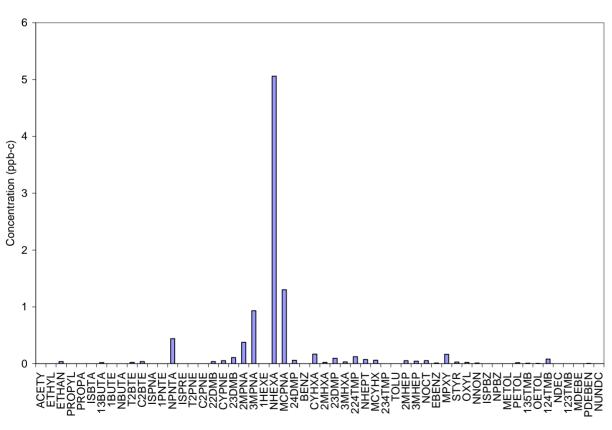


Capitol 3-Hour Source Factor 2



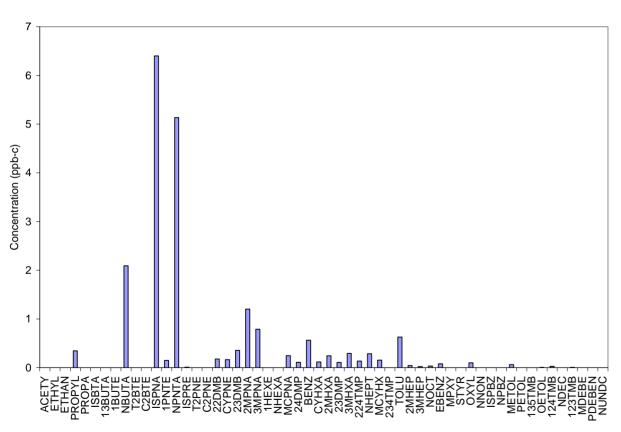


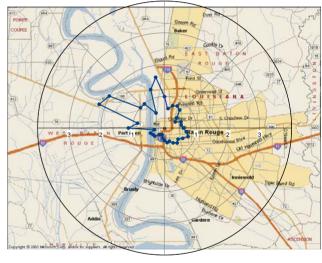




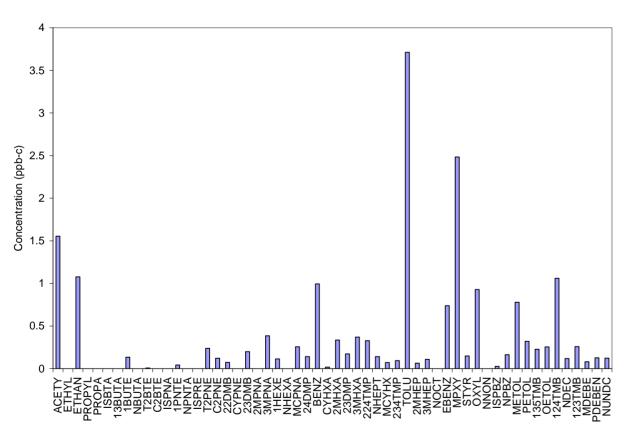


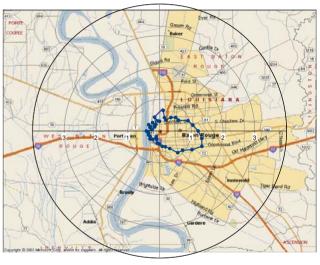




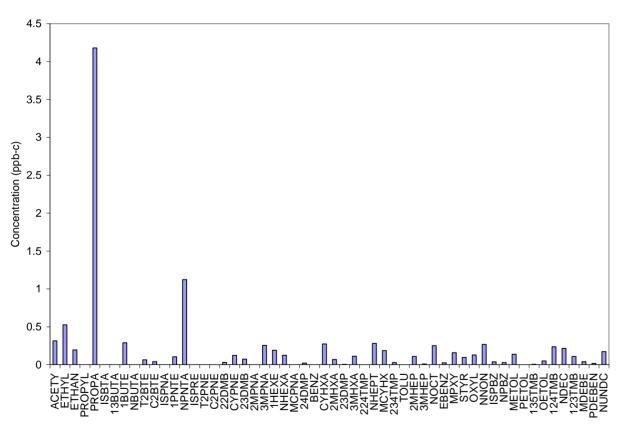


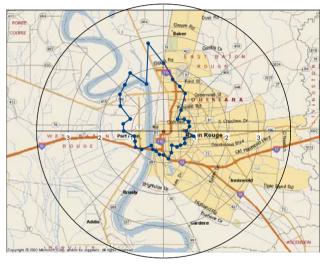




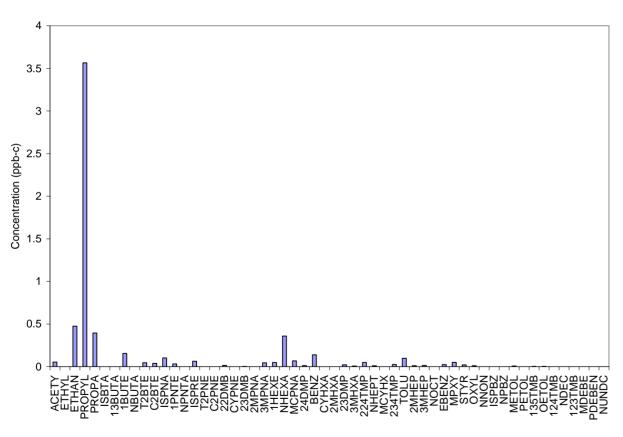


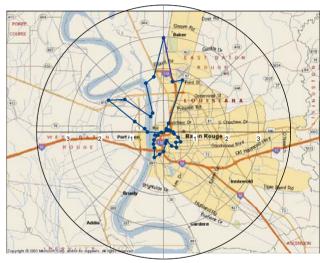




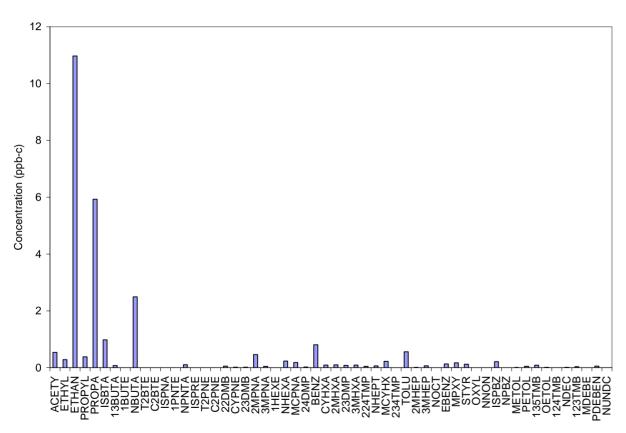


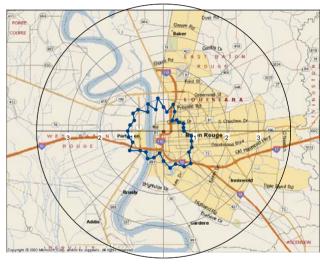




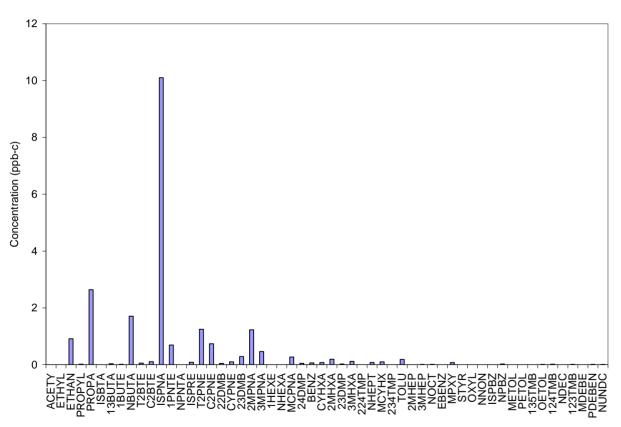


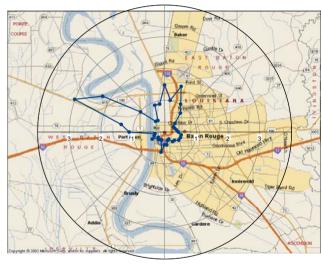




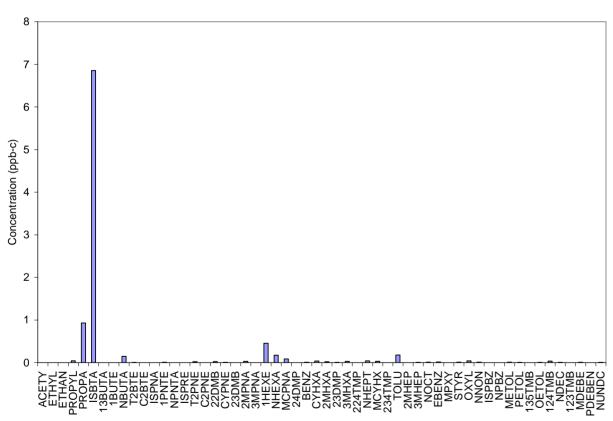


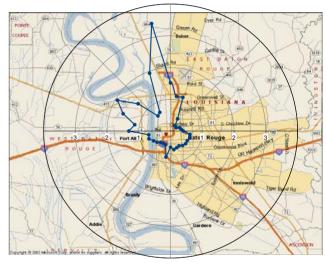




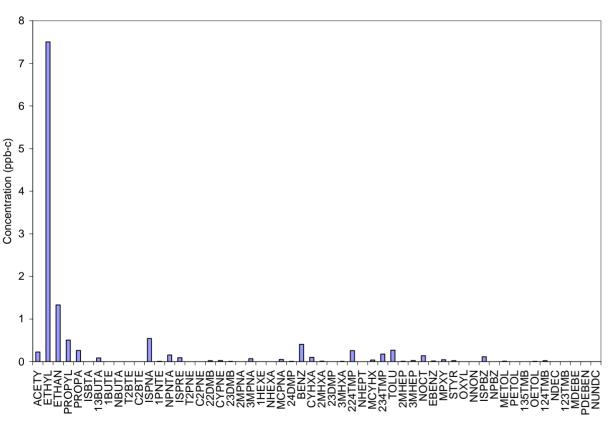


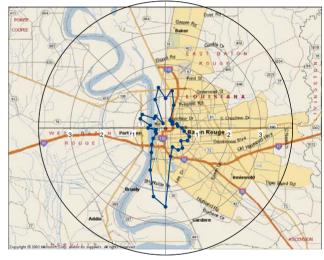




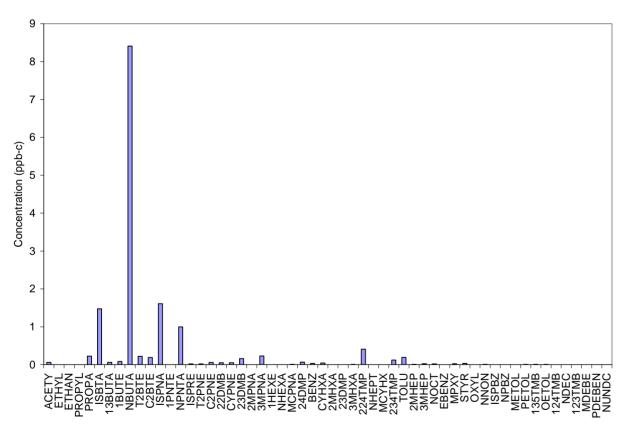


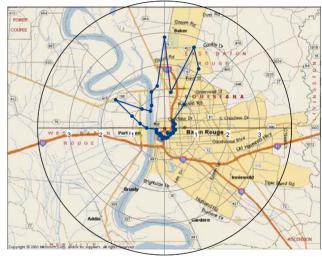




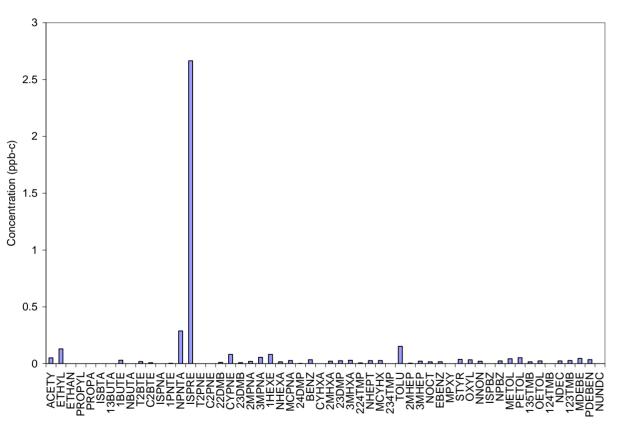
















Capitol 3-Hour A.M. Results (13-Factor Solution)

Factor	Important Species	Average % of Total Mass	Most Important Wind Directions
1	Trimethylpentane, toluene, 2- methylpentane	6%	N,NW,ESE
2	1,3-Butadiene	1%	N,NW,ESE
3	C-6 Alkanes	6%	N,NW
4	Isopentane, n-pentane, n-butane	12%	N, NE, ESE, WNW
5	Toluene, xylenes, benzene, acetylene, ethane	11%	ESE
6	Propane, n-pentane	6%	NW, N
7	Propylene	4%	WNW, N
8	Ethane, propane, n-butane	16%	All (except NE)
9	Isopentane, n-butane, propane, ethane	13%	WNW, NNE
10	Isobutane	6%	WNW, N
11	Ethylene	8%	S,N
12	n-Butane, isopentane, n-pentane, isobutane	9%	NNE, WNW, N
13	Isoprene	3%	E,W



Capitol Strike Sample Results (13-Factor Solution)

Factor	Important Species	Average % of Total Mass	Most Important Wind Directions
1	Toluene, xylene, trimethylpentene,acetylene	9%	SE, W
2	C2-C9 alkanes, xylene,	3%	WNW, NW, ESE
3	C6 Alkanes, propane, ethane, propylene	4%	SE, WNW
4	C5 – C6 alkanes, benzene, toluene	17%	SE, WNW
5	Isobutane	6%	NE, SE, WNW
6	C2-C5 Olefins	3%	NNW, N, NE
7	Ethylene, Isobutane	6%	SE, W, N
8	Propylene, propane, n-butane	5%	SE, WNW, N
9	N-Butane, isopentane	15%	NE, SE, NW
10	1,3-Butadiene	3%	WNW, N
11	Isopentane, n-butane, n-pentane	15%	NE, WNW
12	Ethane, Propane, n-Butane	6%	N
13	Acetylene, ethylene, n-butane, isopentane	7%	All



Port Allen Strike Sample Results (13-Factor Solution)

Factor	Important Species	Average % of Total Mass	Most Important Wind Directions
1	Isopentane, n-pentane, 2- methylpentane	19%	SE
2	Ethane, Propane, isobutane, n-butane	10%	All
3	Isobutane, propane	5%	S
4	Isopentane, n-pentane	7%	SE, S
5	Toluene, xylene n-butane, acetylene, ethylene	7%	N, S
6	Benzene, ethane, propane, toluene, n- pentane	4%	SE, N
7	Ethane, propylene, isobutane, n- butane, trimethylbenzenes	6%	S
8	C4 alkanes and olefins	6%	S
9	N-Butane, isopentane	15%	S, SE, NE
10	N-hexane, methylpentanes, n-butane	8%	S, SE, NE
11	C2-C6 olefins, propane	8%	SE, NE
12	Isopentane, n-pentane, methylcyclohexane	3%	S, SE
13	Ethane, propylene, propane, 1,3- butadiene, styrene	3%	SE, SW



Southern Strike Sample Results (17-Factor Solution)

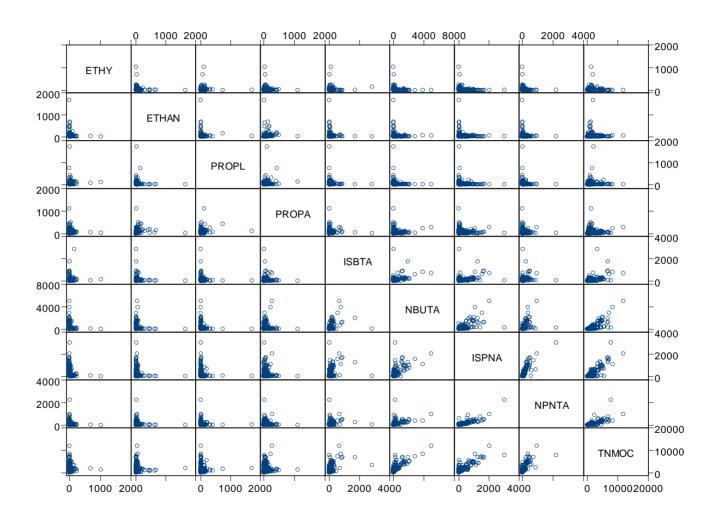
Factor	Important Species	Average % of Total	Most Important Wind Directions
		Mass	
1	Propylene, 13-butadiene	2%	N, NE
2	Isopentane, n-pentane	10%	SE
3	N-butane, benzene	2%	All
4	C3-C9 alkanes, aromatics	3%	All
5	Butanes, isopentane	9%	NE, SE
6	C4-C6 alkanes, pentenes	9%	SE, WNW
7	Butenes, i-butane, propane	3%	S, NW
8	i-pentane, n-pentane, i-butane	13%	S
9	Trimethylpentanes, toluene	3%	NE, SE, W
10	Pentanes, n-butane, toluene	8%	NE, SE, W
11	Pentanes, pentenes	9%	NE, S
12	C6 Alkanes, n-butane	3%	S, SE
13	Acetylene toluene, trimethylbenzenes	2%	NE, S, WNW
14	Ethane, Propane	6%	NE
15	Ethylene	3%	All
16	Propane	6%	SE, NE, WNW
17	Toluene, xylene, 2-methylpentane	4%	All



South Scotlandville Strike Sample Results (17-Factor Solution)

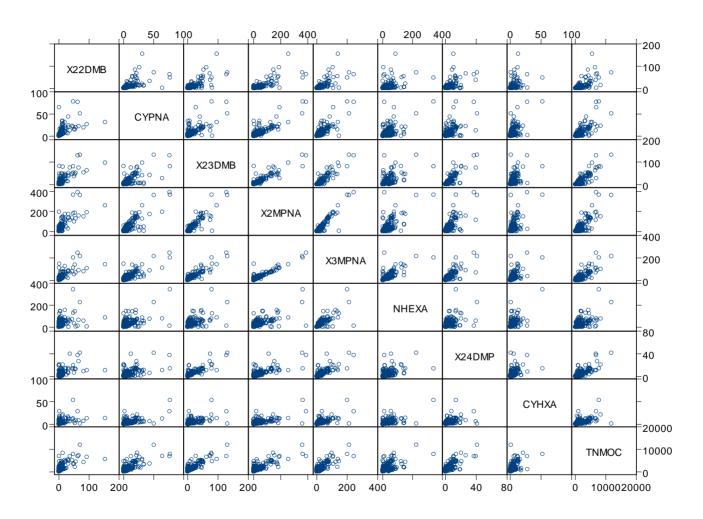
Factor	Important Species	Average % of Total Mass	Most Important Wind Directions
1	N-butane, isopentane	4%	S
2	Propylene, propane	7%	NE, SE
3	Propane, n-pentane, trimethylbenzenes	2%	NE, SE, S
4	Ethylene, isobutane, isopentane	3%	S
5	1,3-butadiene	6%	S
6	Trimethylpentenes, toluene, xylene	3%	S
7	Toluene, xylenes, trimethylbenzenes	2%	SE, S
8	i-pentane, n-pentane	16%	S
9	Isopentane n-pentane, pentenes	12%	S
10	Ethane, Propane	5%	NE, SE
11	C2-C11 alkanes, benzene	3%	S
12	Benzene, toluene, isopentane	4%	SSE
13	Acetylene, toluene, xylene, n-butane	5%	S
14	C6Alkanes	6%	SE
15	C3-C5 Alkanes	12%	S
16	C2-C8 Alkanes, benzene, toluene	3%	S
17	C6 Alkanes, propane, ethane	4%	S

Light Alkanes Correlated More Strongly with TNMOC than did Light Alkenes (Olefins) in North Baton Rouge Strike Samples



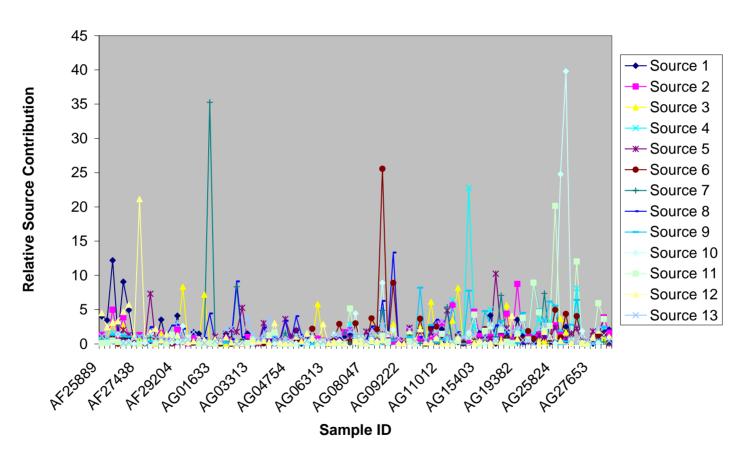


C5-C6 Alkanes Were Also Strongly Correlated with Total NMHC in North Baton Rouge Strike Samples



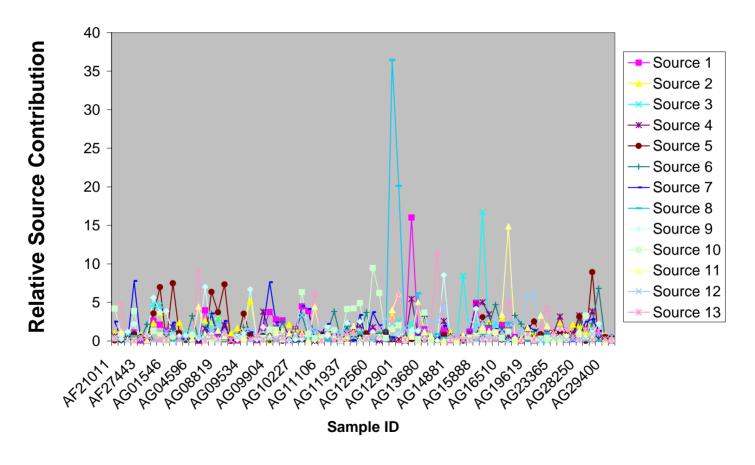


Capitol Strike Samples



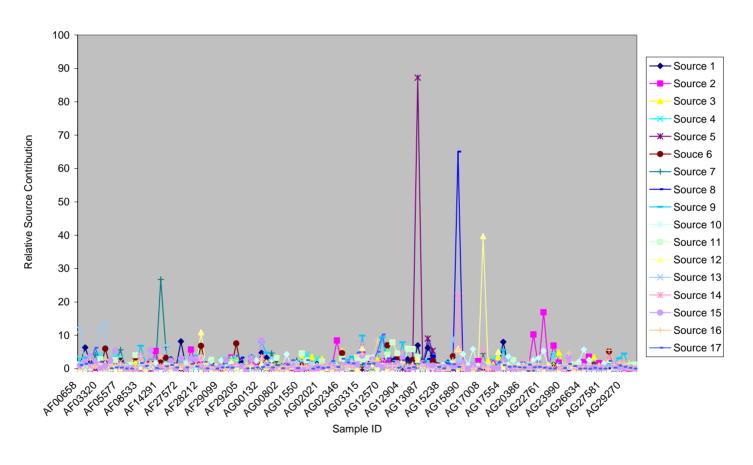


Port Allen Strike Samples



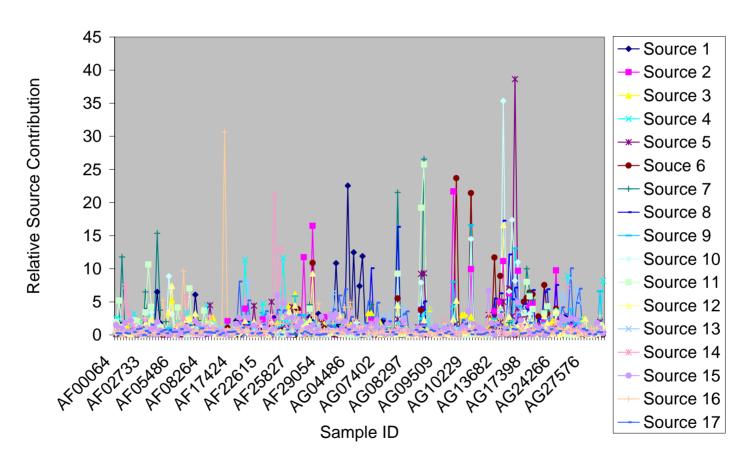


South Scotlandville Strike Samples





Southern Strike Samples





Summary of Source Apportionment Findings (Page 1 of 2)

- Sources of C4-C6 alkanes usually contributed the most of the total carbon mass of strike samples collected at North Baton Rouge sampling sites; these compounds are also most strongly correlated with TNMOC
- Sources of light olefins usually contributed comparatively small amounts to the total carbon mass strike samples collected at North Baton Rouge sampling sites; however, on a reactivity-weighted basis the relative importance of light olefin sources may be greater
- Motor vehicles and always a comparatively small but measurable component of the VOC mixture



Summary of Source Apportionment Findings (Page 2 of 2)

- Biogenic isoprene was 3% of the total carbon mass of 3-hour canister samples collected at the Capitol site during 9:00 p.m. – 8:00 a.m., but was not a measurable component of the North Baton Rouge strike samples
- A background concentration of low molecular weight, low reactivity alkanes made up 5-10% of the total carbon mass of strike samples collected at North Baton Rouge sampling sites and 16% of 3-hour canister samples analyzed from the Capitol site
- The individual source contributions for a few specific strike samples stand out clearly as outliers, suggesting non-routine emissions



Summary and Conclusions Page 1 of 4

- Hour to hour increases of greater than 40 ppb/hr ozone were observed on more than 50% of the 1-hour exceedance days and almost 25% of the 8-hour exceedance days from 1997 – 2004
 - Hour to hour increases of greater than 30 ppb/hr ozone were observed on nearly all 1-hour exceedance days and more than 60% of the 8-hour exceedance days during 1997 – 2004
- Sudden ozone concentration increases such as these occurred mostly on mornings having very low wind speeds and a relative abundance of ozone precursors – VOC and NO_x
- The frequency of occurrence for sudden ozone increases was greatest at the Port Allen monitor and least at outlying monitoring sites
- A decreasing trend in the frequency of occurrence of sudden ozone concentration increases is apparent



Summary and Conclusions Page 2 of 4

- Average VOC reactivity was greatest for samples collected at Port Allen and other sampling sites near the Mississippi River in North and Central Baton Rouge
- Ethylene, propylene, and isoprene accounted for almost 40 of the reactivity on average; although the relative importance of these compounds varied from site to site and from sample to sample
- Isoprene had the greatest site to site variability; it accounted for 30% of the total reactivity at Pride but only 3% at South Scotlandville
 - Surprisingly when compared with nearby sites, isoprene accounted for 15% of the reactivity at Port Allen
- Compounds that are considered HRVOV in Baton Rouge (i.e., ethylene, propylene, isomers of butene, butadiene, toluene, and xylene accounted for slightly less than one-half the total reactivity on average
- The average reactivity decreased from 2002 2004 at most sites; although, no long-term trend is apparent



Summary and Conclusions

Page 3 of 4

- Monitored levels of NOx and HRVOC tend to vary with wind direction in a pattern that is consistent with the relative directions of nearby and regional emissions sources
- On average, the monitored HRVOC/NO_x ratios were several times (roughly an order of magnitude) greater than the HRVOC/NO_x derived from 2003 emissions estimates
- This does <u>not</u> mean that actual emissions are an order of magnitude greater than reported emissions, because of uncertainties and limitations of the analysis, but does suggest a need for further investigation; especially if new ozone modeling is being planned for Baton Rouge



Summary and Conclusions

Page 4 of 4

- Sources of C4-C6 alkanes usually contributed the most of the total carbon mass of strike samples collected at North Baton Rouge sampling sites; these compounds are also most strongly correlated with TNMOC
- Sources of light olefins usually contributed comparatively small amounts to the total carbon mass strike samples collected at North Baton Rouge sampling sites; however, on a reactivity-weighted basis the relative importance of light olefin sources may be greater
- The individual source contributions for a few specific strike samples stand out clearly as outliers, suggesting non-routine emissions



Recommendations

(Page 1 of 2)

- Statistical Analysis of Ozone Spikes
 - An analysis of NO_x-limitation and VOC-limitation indicators would help to more precisely define the relative importance of NO_x and VOC in contributing toward sudden ozone increases and exceedances of the ozone NAAQS

VOC Reactivity

- Increasing the sampling frequency at Port Allen to 8 per day (3-hour samples), at least for a short-term study, would help determine whether comparatively high levels of isoprene measured there were from industrial sources or biogenic
- Triggering sample collection based the rate of ozone increase rather than TNMHC would be more useful toward identifying the VOC most directly related to sudden ozone increases



Recommendations

(Page 2 of 2)

Emissions Inventories

 A comprehensive review of VOC emission inventory practices, particularly with regard to speciation is needed to investigate potential emissions estimating biases inferred from ambient monitoring results

Source Apportionment

- A more comprehensive analysis of the sensitivities to model inputs and formulation plus consultation with LDEQ emissions inventory staff or industry stakeholders would help to better define the source factors of greatest importance
- Performing source apportionment on reactivity basis would be helpful toward identifying the sources that have the greatest ozone formation potential
- A detailed analysis of source contribution variability would help assess the importance of routine vs. episodic emissions

